PRACTICAL
ORGANIC CHEMISTRY.

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BY

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PREFACE.

We have much pleasure in recommending this little book to the notice of advanced students of chemistry. Any course of Practical Organic Chemistry leading up to original work in this branch of the science, must mainly consist in the careful preparation of a well-selected series of organic compounds. Dr. Julius Cohen has in the following pages collected such a series, and we feel confident that this work, filling, as it does, a lacuna in our English chemical literature, will prove most useful alike to the Professors, Demonstrators, and Students of our science.

Henry E. Roscoe.

C. Schorlemmer.

AUTHOR'S PREFACE.

THE author wishes it to be clearly understood that the book is only intended for the use of students who are undergoing or have undergone a substantial course of instruction in the principles of organic chemistry. Its primary purpose is that of a laboratory guide, and its use should be supplemented by reference to some of the large text-books, as well as to the original sources of chemical literature mentioned at the head of each preparation. For convenience of immediate reference, and in the hope of emphasising some of the important facts, an Appendix is added, containing some notes explanatory of the theoretical importance of the reactions involved in the preparations.

The preparations have been selected and arranged with the object of illustrating the relationship existing between certain groups of organic bodies, as well as their characteristic reactions.

The usual arrangement of fatty before aromatic compounds has been reversed for the reason that those of the latter, which have been selected, offer fewer difficulties to the beginner.

For valuable assistance given him by Professor Schorlemmer and Professor Smithells, to Professor Emil Fischer, to whom he is indebted for the details of some of the preparations, to Dr. W. H. Perkin, junior, and others, the author's best thanks are due.

TO THE STUDENT.

Before beginning the preparation, read the recent literature on the subject, reference to which will be found at the head of the preparation, and refer to it in your text-book. A few explanatory notes are added in the Appendix. Weigh the quantities prescribed on a rough chemical balance. Note the yield of the product in each case, and compare it with the quantity theoretically obtainable.

OWENS COLLEGE, *April*, 1887.

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PART I.

PART II.

ABBREVIATIONS.

ANN. CH. PHARM. = Liebig's *Annalen der Chemie und Pharmacie*, vol. i. (1832), 8 supplements, 4-5 vols. annually.

ANN. CH. PHYS. = *Annales de Chimie et de Physique*, 1st series (1789-1815), 2nd series (1816-1840), 3rd series (1841-1863), 4th series (1864-1873), 5th series, from 1873. 3 vols. annually.

BER. ... ... = *Berichte d.r deutschen chemischen Gesellschaft*, vol. i. (1868). 1 vol. annually.

BERZ. JAHRESB. = *Jahresbericht uber die Fortschritte der physischen Wissenschaften*, J. Berzelius (1821-1847).

BULL. SOC. CHIM. = *Bulletin de la Société Chimique de Paris*, under the title of *Répertoire de Chimie pure et appliquée*, vols. i.-v. (1858-1863). Since then under the first title. 2 vols. annually.

CHEM. SOC. J. ... = *Journal of the Chemical Society*, vols. i.-xxviii. (1848-1875). 1 vol. annually; since 1876 (vols. xxix.-xxx.) 2 vols. annually.

COMPT. REND. . . = *Comptes rendus des Séances de l'Académie des Sciences*, vol. i. (1835). 2 vols. annually.

JAHRESB. .. ... = *Jahresbericht über die Fortschritte der Chemie* (Ricker), vol. i. (1847-1848). 1 vol. annually.

ABBREVIATIONS.

JOURN. PRAKT. CH. = *Journal fur praktische Chemie*, vols. i.-cviii. (1834-1869). 3 vols. annually. Neue Folge since 1870. 2 vols. annually.

MONATSH. ... ... = *Monatshefte für Chemie*, vol. i. (1880). 1 vol. annually.

PHIL. MAG. ... = *Philosophical Magazine*, vol. i. (1798).

PHIL. TRANS. ... = *Philosophical Transactions of the Royal Society*, vol. i. (1665). 1 vol. annually.

PROC. ROY. SOC. = *Proceedings of the Royal Society*, vol. i. (1847). 1 to 2 vols. annually.

POGG. ANN. ... = *Poggendorff's Annalen der Physik und Chemie*, 160 vols. (1824-1877). Neue Folge, edited by J. Wiedemann, vols. i.-ii. (1877). 3 vols. annually.

ZEITSCHR. F. CH. = *Zeitschrift für Chemie* (Beilstein, Fittig, and Hubner), vols. i.-vii. (1865-1871).

PART I.

1. PURIFICATION OF ALCOHOL.

Commercial absolute alcohol (ethyl alcohol), obtained by rectifying crude spirits of wine over quicklime, is seldom free from water. The alcohol may be further dehydrated by allowing it to stand for twenty-four hours in a flask half filled with freshly-burnt and coarsely powdered quicklime, and then distilling off on the water-bath. The apparatus for this purpose is represented in Fig. 1. The alcohol if pure boils constantly at 78°—79°. The temperature is indicated by a thermometer inserted through the cork in one limb of a T-piece *a*, the other end of which is fitted vertically into the flask. The side limb is bent through a small angle and passes into the inner tube of the condenser. The bulb of the thermometer is adjusted below this side limb, so that it is heated by the ascending vapours of the boiling liquid.

BOILING-POINT DETERMINATION.—A correct determination of the boiling-point of a liquid is made with a standard thermometer, correction being made for barometric pressure, and, if

necessary, for the thread of mercury which projects above the vessel. For the latter the formula given in a foot-note on p. 25 may be used. It is, however, preferable to use a short thermometer, so that the mercury column is entirely immersed in the vapour.

Methylated spirit is a mixture of 9 parts spirit of wine and 1 part purified wood-spirit, and contains

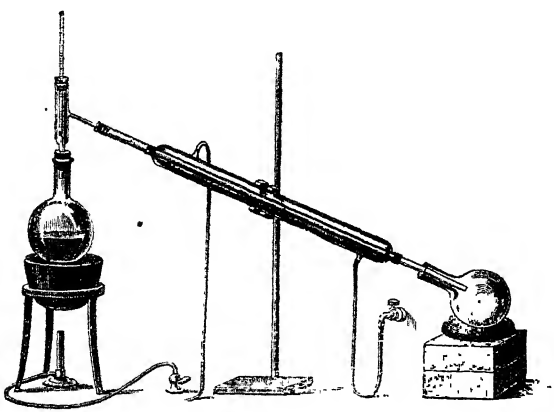


FIG. 1.

in addition to ethyl and methyl alcohols, water, fusel oil, acetaldehyde, and acetone. It may be freed from aldehyde and acetone by boiling with 3—4 per cent. solid caustic potash on the water-bath with reflux condenser for an hour (Fig. 2), and then distilling off on the water-bath. It is freed from water

by distilling once or twice over fresh quicklime in the manner described. Purified methylated spirit may generally replace the more expensive ethyl alcohol as a solvent.[1]

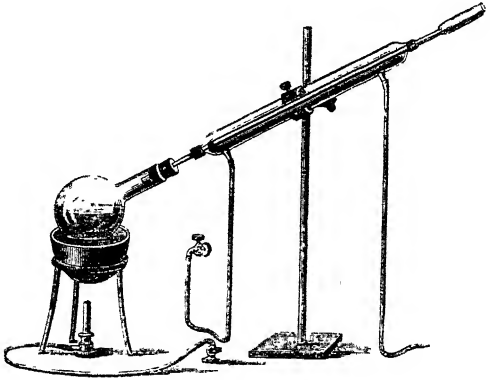


FIG. 2.

2. PURIFICATION OF ETHER.

Pure commercial ether, prepared from ethyl alcohol (p. 100) and free from water and alcohol, has no action upon sodium. Its specific gravity at 15° is ·720. If there is a slight evolution of hydrogen on

[1] COMMERCIAL METHYL ALCOHOL, obtained by purifying wood spirit, is now [illegible] nearly free from acetone, and, after purification with [illegible], may also replace ethyl alcohol as a solvent.

introducing a small piece of sodium, on adding more sodium the action soon ceases and the ether is then anhydrous. If, on the other hand, the action is brisk, the ether must be left in contact with small pieces of fused calcium chloride for twenty-four hours, poured off, and a few thin slices of sodium introduced. The vessel is then closed by a cork, through which an open chloride of calcium tube is inserted to allow any hydrogen to escape and to prevent absorption of moisture.

Methylated ether, prepared from methylated spirit by the same process as the ethyl ether, consists of a mixture of diethyl, ethyl methyl, and dimethyl ethers, and contains usually alcohol and water. For extracting substances from aqueous solutions the ether may be employed without further purification. To free it from alcohol it is shaken up repeatedly with small quantities of water. The water dissolves out the alcohol and forms a layer at the bottom of the liquid, and is drawn off by means of a separating funnel. The ether, separated as carefully as possible from water in this way, is dehydrated over fused calcium chloride, and sodium, as described above. It should not give the *iodoform* reaction. (*See* Appendix.)

N.B.—*In cases where ether is used great care should be taken, that no flame is in the neighbourhood of the liquid.*

3. PURIFICATION OF BENZENE.

Pure commercial benzene, obtained from coal-tar naphtha, should distil within one degree (80°—81°) and solidify completely when cooled to 0°. Other tests are as follows: Shaken with concentrated sulphuric acid for a few minutes, the acid should not darken, and a drop of bromine water should not be immediately decolorised. A single distillation over a few small pieces of sodium which absorb any traces of water, is usually a sufficient purification. If the benzene impart a brown or black colour to sulphuric acid it must be repeatedly shaken with about 20 per cent. of the acid until the latter becomes only slightly yellow on standing. This is done in a stoppered separating funnel, and after shaking for a minute the mixture is allowed to settle and the lower layer of acid drawn off. The benzene is then shaken two or three times with water to free it from acid, carefully separated from the aqueous layer and allowed to remain in contact with pieces of fused calcium chloride until the liquid becomes clear. It may then be frozen in ice, and any liquid (carbon bisulphide, paraffins) carefully drained off and the benzene finally distilled over sodium.

Commercial 50 *per cent. and* 90 *per cent. benzene* are mixtures of benzene and larger or smaller quantities of its higher boiling homologues, viz. toluene (110°) and the xylenes (137°—143°). The benzene may be separated by *fractional distillation.*

It is often possible to separate almost completely by a single distillation two liquids occurring together in a mixture when their boiling-points lie widely apart. The more volatile liquid first passes over, the temperature suddenly rises, and the higher boiling liquid distils. Thus, in the separation of ethyl benzene (p. 16 from its ethereal solution, the ether (B. P. 35°) distils off almost completely at the temperature of the water-bath, leaving behind the ethyl benzene (B. P. 134°). It is otherwise when a liquid consists of a mixture of bodies boiling at temperatures not very far removed from one another, especially in the case of homologous compounds such as occur in petroleum and coal-tar naphtha. One distillation suffices only to produce very partial separation of the different substances, a portion of the less volatile liquid being carried over in the first distillate together with the more volatile body, the temperature gradually rising throughout the distillation. In order to effect separation of the several substances in a case of this kind recourse is had to the method of fractional distillation.

The liquid is distilled in a round-bottomed flask over wire-gauze or, better, in a fusible metal bath with a thermometer so placed that the temperature of the vapour of the boiling liquid is indicated, *i.e.* with the bulb just below the side tube of the fractionating column (Fig. 3). As the temperature gradually rises the distillate, which passes over between every

3°, 5°, or 10°, as the case may require, is collected in separate flasks. These separate portions are called fractions. Each of these fractions when submitted to a second distillation is usually found to begin to boil at a temperature lower than that indicated in the first instance, so that it is possible in this way to subdivide

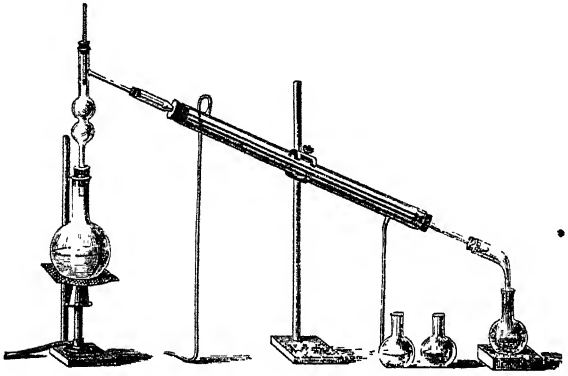


FIG. 3.
Distilling apparatus with Wurtz's fractionating column.

each fraction into a portion of lower boiling-point, and a portion of higher boiling-point, and the process is continued until certain of the fractions have a nearly constant boiling-point. If the vapour, which rises from the boiling liquid to be fractionated, undergoes slow cooling before reaching the condenser, the less

volatile portion carried upwards with the more volatile vapour is partially condensed. If this is allowed to flow back into the flask only the lower boiling portion passes into the condenser, and the separation is more

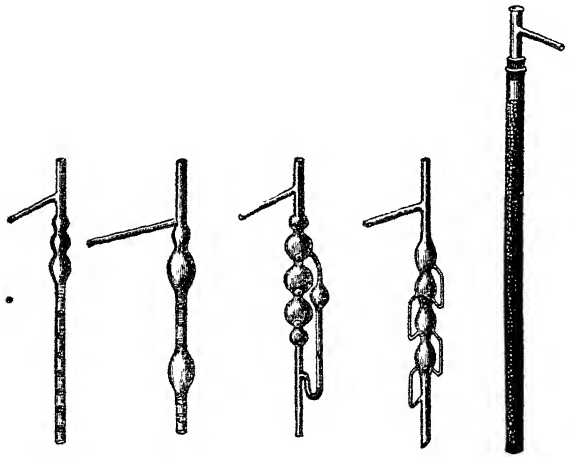


FIG. 4. FIG. 5 FIG. 6. FIG. 7. FIG. 8.

The apparatus of Linnemann (Figs. 4 and 5) contains a series of wire gauze cups, that of Glinsky (Fig. 6) and Lebel and Henninger (Fig. 7) has in addition a side tube, down which condensed vapour flows. Hempel's apparatus (Fig. 8) is a long wide glass tube filled with small glass beads

rapid and effective. Several forms of apparatus have been devised on this principle (*see* Figs. 4—8).[1]

[1] The apparatus of Linnemann and of Hempel have been found to give very good results with low boiling-liquids (Kreis ; *Ann. Ch. Pharm.* 224, 259).

Fit up an apparatus as shown in Fig. 3 with fractionating column, and distil 200 c.c., 50 per cent. or 90 per cent. benzene at a regular speed, so that the drops falling from the end of the condenser may be readily counted. Collect the distillate between every five degrees in separate flasks. Redistil each of these fractions in order, adding the next to the residue of the previous one in the distilling flask, and collect portions boiling below 85° and above 105° between every two or three degrees. Redistil the fractions below 85° and above 105° as before, and collect between every two degrees. It will be found that by repetition of the process the liquid is gradually separated into two large fractions consisting chiefly of benzene and toluene and a number of smaller intermediate fractions. The following table gives the volume in c.c. and the boiling-points of the fractions obtained by this method from 200 c.c. 50 per cent. benzene, each table denoting a complete series of fractionations.

I.

A. 71·5-85°	B. 85-90°	C. 90-95°	D. 95-100°	E. 100-105°	F. 105-110°	G. 110-115°	Residue.
19 c.c.	53 c.c.	26 c.c.	15 c.c.	13 c.c.	17 c.c.	21 c.c.	33 c.c.

II.

	A′. below 79°.	B′. 79-81°	C′. 81-85°	D′. 85-105°	E′. 105-108°	F′. 108-110°	Residue.
A.	5 c.c.	...	...	...	...	...	...
Added B.	...	42 c.c.	(10 c.c.*)	...	...	. .	...
Added C.	. .	...	(9 c.c.*)	...	...	...	...
Added D. E.	...	...	...	50 c.c.	...	...	. .
Added F.	...	...	...	...	(11 c.c.*)	...	...
Added G.	...	...	. .	...	...	22 c.c.	42 c.c.
*Refractioned C′.	...	12 c.c.	7 c.c.	...	...	...	...
E′.	...	...	...	...	6 c.c.	5 c.c.	...
	5 c.c.	54 c.c.	7 c.c.	50 c.c.	6 c.c.	27 c.c.	42 c.c.

The fraction 79°—81° is further purified in the manner already described.

PREPARATION I.

MONOBROMOBENZENE, C_6H_5Br.

LITERATURE.—Couper (1857), Ann. Ch. Pharm. 104, 225; Fittig (1862), Ann. Ch. Pharm. 121, 361; Riche (1862), Ann. Ch. Pharm. 121, 360. Michaelis (1876) Ann. Ch. Pharm. 181, 289.

50 grms. benzene.
105 grms. bromine.

Fifty grms. benzene and 105 grms. bromine are poured into a round-bottomed flask of about 300 c.c. capacity fastened by a stout piece of india-rubber tubing to the end of a condenser, which projects into the neck of the flask (Fig. 9). The mixture is gently

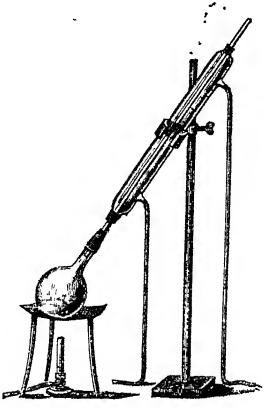


FIG. 9.

heated over wire-gauze with a small flame* until the evolution of hydrobromic acid fumes from the top of the condenser have nearly ceased. The product,

* Denotes that the operation must be conducted in a draught cupboard or in the open air.

which has a deep red colour, is allowed to cool and dry air aspirated through it in order to drive off dissolved hydrobromic acid. The unattacked benzene is then distilled off on the water-bath. On the addition of dilute caustic soda solution to the residual liquid monobromobenzene settles to the bottom of the vessel as a heavy oil. On shaking in a stoppered separating funnel the excess of bromine is dissolved out, and the liquid loses gradually its red colour. The oil is allowed to settle and carefully drawn off from below. It is shaken repeatedly with water in a similar manner, and finally dehydrated over a few pieces of fused calcium chloride.

The clear liquid decanted from the calcium chloride is distilled over wire-gauze, a thermometer being inserted into the neck of the flask. A small quantity of benzene passes over and the temperature then rises rapidly, the chief portion of liquid boiling between 150° and 155°, which is separately collected. The colourless distillate is nearly pure bromobenzene. Small quantities of para-dibromobenzene, which are formed in the above reaction, remain in the distilling flask, and solidify on cooling. This compound may be dissolved out with ether or warm alcohol, from which it crystallises on evaporation. It is to be obtained pure by one or two recrystallisations from alcohol (prismatic crystals, melting point 89°, boiling point 219°).

Reaction (expressed in the form of equation):

$$\underset{\text{Benzene.}}{C_6H_6} + 2Br = \underset{\text{Monobromobenzene.}}{C_6H_5Br} + HBr$$

$$C_6H_5Br + 2\,Br = \underset{\text{Dibromobenzene.}}{C_6H_4Br_2} + HBr$$

Properties.—Colourless liquid; boiling-point 154°—155°; specific gravity 1·5176 at 0°.

PREPARATION II.

ETHYL BENZENE, C_8H_{10} = [illegible]

LITERATURE.—Fittig (1864), Ann. Ch. [illegible] 131, 303; Fittig, König (1867), Ann. Ch. Pharm. 144, 277.

60 grms. bromobenzene.
52 „ ethyl bromide (see p. 95).
26·5 „ sodium.

A quantity of pure ether (about twice the volume of the mixed phenyl and ethyl bromides) is poured into a round-bottomed flask, about 1 litre capacity, connected with a reflux condenser. 26·5 grms. clean sodium cut into thin slices are added to the ether, and when all evolution of hydrogen has ceased the flask is immersed in a vessel of water which is cooled by the addition of ice (Fig. 10). The mixture of 60 grms. bromobenzene and 52 grms. ethyl bromide, both of which must be perfectly anhydrous, is poured

into the flask. The reaction is allowed to commence spontaneously, the fact being indicated by the sodium becoming darker in colour and sinking to the bottom of the vessel. Although the flask is allowed to remain in the outer vessel, and is cooled by water and ice, the heat evolved in the reaction often causes the ether

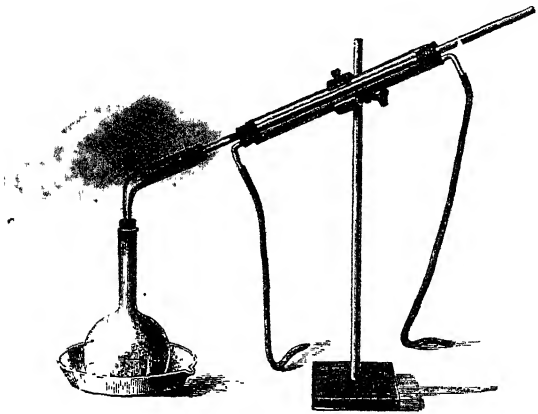


FIG. 10.

to boil. The flask is, therefore, not removed from this vessel until the reaction is over. The ether is then distilled off on the water-bath, and the ethyl benzene is driven over as quickly as possible by using a naked flame, the vessel being first gently heated round the sides, and finally more strongly from below, until no

more liquid distils. The distillate, containing ether and benzene, is rectified, and the portion boiling at 132°—135° collected.

$$\underset{\text{Bromobenzene}}{C_6H_5Br} + \underset{\text{Ethylbromide}}{C_2H_5Br} + 2\,Na = \underset{\text{Ethylbenzene.}}{C_6H_5.C_2H_5} + 2\,Na\,Br$$

Properties.—Colourless liquid; b. p. 134°; sp. gr. ·8664 at 22·5°.

PREPARATION III

NITROBENZENE, C

LITERATURE.—Mitscherlich (
12, 305; Mulder (1840), Journ. prakt.

50 grms. benzene.
100 ,, conc. nitric acid, sp. gr. 1·42.
150 ,, conc. sulphuric acid.

A well-cooled mixture of 100 grms. conc. nitric acid, and 150 grms. conc. sulphuric acid is slowly added from a tap-funnel to 50 grms. benzene contained in a flask of about ½ litre capacity.* The contents of the flask are meanwhile *well shaken.* Nitrous fumes are evolved, and a considerable amount of heat developed. Care must be taken that the temperature does not exceed 40°—50° by immersing the flask, if necessary, in cold water. The nitrobenzene separates out as a brown, oily layer on the surface of the acid

liquid. When the acid has all been added—an operation which lasts about half an hour—the mixture is heated for about twenty minutes on the water-bath and again well shaken. The contents of the flask on cooling are poured into a stoppered-separating funnel, the lower layer of acid removed, and the nitrobenzene washed free from acid by shaking once or twice with water, then with dilute carbonate of

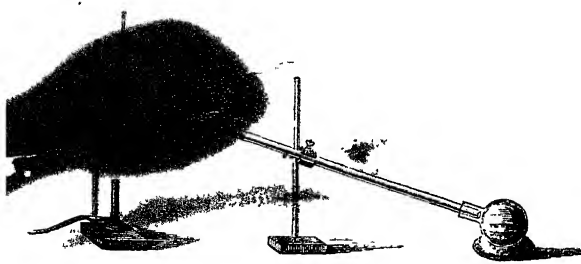


FIG. 11.

soda solution, and again with water, the oil being each time withdrawn from the *bottom* of the vessel. The nitrobenzene, separated as carefully as possible from water, is allowed to stand over a few pieces of fused calcium chloride, and shaken occasionally until the liquid is perfectly clear.

The yellow liquid is decanted from the calcium chloride and distilled in a dry distilling flask, the side tube of which fits into a long straight condensing

tube (Fig. 11). At first a little benzene passes over, the temperature then rises, and the nitrobenzene distils at · 204°—207°, and is separately collected. The brown residue contains a small quantity of dinitrobenzene.

$$\underset{\text{Benzene}}{C_6H_6} + HONO_2 = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + H_2O$$

The function of the sulphuric acid is that of a dehydrating agent, taking up the water formed in the reaction.

Properties.—Light yellow liquid, smelling of bitter almonds; b. p. 206°—207°; sp. gr. 1·208 at 15°; it solidifies at + 3°; insoluble in water, soluble in alcohol, ether, benzene, and conc. nitric acid.

PREPARATION IV.

ANILINE, $C_6H_7N = C_6H_5.NH_2$.
(*Amidobenzene, Phenylamine.*)

LITERATURE.—Unverdorben (1826), Pogg. Ann. 8, 397; Runge (1834), Pogg. Ann. 31, 65; Fritsche (1840), Ann. Ch. Pharm. 36, 84, and 39, 76; Zinin (1842), Ann. Ch. Pharm. 44, 283; Hofmann (1844), Ann. Ch. Pharm. 47, 37; Roussin (1861), Jahresb. 643.

60 grms. nitrobenzene.
195 „ tin (granulated or in powder).
350 „ conc. hydrochloric acid.

Sixty grms. nitrobenzene and 95 grms. granulated or powdered tin, are placed in a flask of about 1 litre

capacity. The mixture is heated for a few minutes on the water-bath and 350 grms. conc. hydrochloric acid are gradually added in small quantities, the amount being regulated by the reaction, which should proceed steadily. If the contents of the flask begin to boil up violently, the flask is cooled in water until the reaction has somewhat slackened. When nearly the whole of the tin has dissolved, the flask is transferred to the water-bath and heated for about an hour. The liquid now contains no drops of oil and the smell of nitrobenzene should have disappeared. The contents of the flask, which on cooling solidify to a crystalline mass (a double salt of stannic chloride and aniline hydrochloride) are diluted with water, and strong caustic soda solution added until the stannic oxide, which is first precipitated, nearly redissolves. The aniline, which separates out as a dark-coloured oil, is distilled with steam. For this purpose the apparatus shown in Fig. 12 is employed. The mixture containing the aniline is placed in a flask (*B*) connected with a condenser, the flask being somewhat inclined to prevent liquid spirting into the neck and being carried over into the receiver. The flask is heated gently on a sand-bath. Steam is passed in from a second flask (*A*) containing water by a tube which reaches below the level of the liquid to be distilled. A straight vertical tube open at both ends and dipping below the level of the water, prevents the aniline mixture rushing back when the lamp is withdrawn

from under the boiling water. Aniline and water collect in the receiver, the former as an almost colourless oil. When no further condensation of oil is observed, the distillation is discontinued and the oil extracted from the distillate by shaking the liquid in a separating funnel two or three times with small quantities (50 c.c.) of ether. The ethereal solution separated as far as possible from water is further

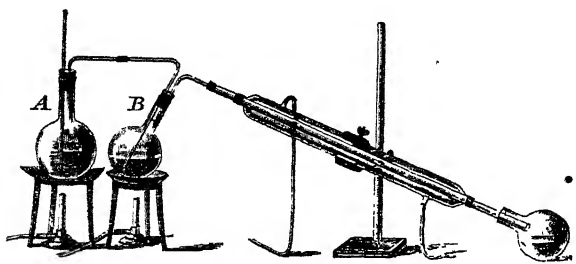


FIG. 12.

dehydrated by adding a few pieces of solid caustic potash. The clear liquid is decanted into a distilling flask and the ether distilled off on the water-bath, until nothing more passes over. The residue is distilled over wire gauze. Aniline distils at 181°—182° and has usually a faint amber colour.

$$\underset{\text{Nitrobenzene.}}{2C_6H_5NO_2} + 3Sn + 12HCl = \underset{\text{Aniline.}}{2C_6H_5NH_2} + 3SnCl_4 + 4H_2O$$

Properties.—Colourless, highly refracting liquid, which quickly darkens in colour; b. p. 182°; sp. gr. 1·0265 at 15°. With bleaching powder solution, a drop of the oil gives a blue colour; on heating a few drops of the base with a little alcoholic potash and a drop of chloroform in a test-tube phenylcarbamine is formed, a substance possessing an intolerable smell (Hofmann's reaction for primary amines). If a few drops of conc. sulphuric acid be added to a drop of aniline and then a few drops of a solution of potassium bichromate, a blue colour is produced.

PREPARATION V.

ACETANILIDE, $C_8H_9NO = C_6H_5.NH.CO.CH_3$.
(*Phenylacetamide.*)

LITERATURE.—Gerhardt (1853), Ann. Ch. Phys. (3) 37, 328; G. Williams (1864), Chem. Soc. J. 2, 106.

25 grms. aniline.
25 „ glacial acetic acid.

Twenty-five grms. aniline and 25 grms. glacial acetic acid are mixed in a retort or flask of about 250 c.c. capacity connected with a straight upright tube or air condenser (Fig. 13) and boiled for about six hours. The liquid on cooling solidifies. The

acetanilide while warm is therefore at once poured into a quantity of cold water. It may be recrystallised from dilute alcohol and forms colourless tabular crystals, the purity of which may be ascertained by observing the melting-point.

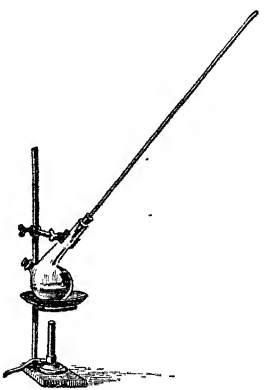


FIG. 13.

Melting-point determination.—For this purpose the following apparatus is used (Fig. 14). A small sample of the finely powdered substance, dried in a desiccator over sulphuric acid, is introduced into a fine capillary tube sealed at one end. The substance is shaken to the bottom of the tube by gently tapping the sealed end. This portion of the tube attached to a thermometer by an india-rubber ring is immersed in conc. sulphuric

acid contained in a small beaker, which it half fills. The beaker is gently heated over a small flame until the substance melts. The temperature is then noted. The lower end of the thermometer bulb and the sealed end of the capillary tube must stand at the same level in the liquid (about ½ to 1 cm. from the

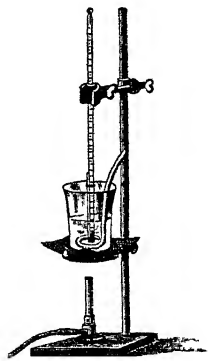


FIG. 14.

bottom of the vessel). The liquid is maintained at a uniform temperature whilst being heated by stirring gently with a glass rod the lower end of which is bent at right angles and then formed into a ring. By slowly raising the temperature of the liquid the melting-point of the substance may be readily observed. The substance is allowed to cool and is reheated. In

this way the freezing and melting-points (uncorrected)[1] may be repeatedly determined. The substance, if pure, melts completely and suddenly within one or two degrees; if impure the liquefaction is protracted and the melting-point usually too low. According to the temperature at which the substance melts, water, paraffin, or oil may replace the sulphuric acid in the bath used.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Acetic Acid}}{CH_3COOH} = \underset{\text{Acetanilide.}}{C_6H_5NH(CH_3CO)} + H_2O$$

Properties.—Rhombic plates; m. p. 112°; b. p. 295°; on boiling with caustic potash or strong hydrochloric acid it is resolved into acetic acid and aniline.

[1] The following expression gives the correction required by the difference of temperature of the column of mercury outside the vessel, and is added to the observed temperature.

$$N(T-t)\cdot 000154$$

where T = apparent temperature in degrees
t = temperature of a second thermometer, the bulb of which is placed at half the length of N above the vessel
N = length of the mercury column in degrees from above the vessel to T
·000154 = apparent expansion of mercury in glass.

In the new apparatus of Roth (Ber. 19, 1970) this correction is obviated.

PREPARATION VI.

ORTHO- AND PARA-NITRACETANILIDE, $C_8H_8N_2O_3$ = $C_6H_4{}^{(1)NH\cdot C_2H_3O(1)}_{(2)NO_2\quad\quad(4)}$

LITERATURE.—Körner (1876), Chem. Soc. J. 14, 209; Witt (1875), Ber. 8, 144; Grethen (1876), Ber. 9, 775; Beilstein, Kurbatow (1879), Ann. Ch. Pharm. 197, 83.

12 grms. acetanilide.
40 ,, fuming nitric acid, sp. gr. 1·5.

Twelve grms. powdered acetanilide are added slowly and in small quantities to 40 grms. fuming nitric acid contained in a beaker cooled in water. The mixture must not be allowed to become warm, otherwise a violent reaction occurs and the nitro-compounds decompose. When the acetanilide has been added, the liquid has a deep red colour. It is now poured upon pounded ice or snow when the para- and a small quantity of ortho-compound separate out as a yellow curdy precipitate. This is rapidly filtered at the pump and washed once or twice with cold water. The filtrate, which has a red colour and contains the chief portion of the ortho-compound, is removed, the residue is again washed with water, well pressed, and dried at 100°. In order to dissolve out any ortho-nitracetanilide from the para-compound, the

dried substance is powdered and washed with cold chloroform until the washings are nearly colourless. The residue on the filter has a light yellow colour, and crystallises from alcohol in almost colourless needles.

The red-coloured filtrate containing the ortho-compound is extracted two or three times with chloroform, which dissolves it, forming a deep red layer at the bottom of the vessel. This is carefully separated. On distilling off the chloroform on the water-bath a red oil remains, which is poured, while still warm, into a beaker. On cooling it solidifies; more quickly if the bottom of the vessel is scratched with a glass rod. The crystals are spread upon a porous plate to drain and then dissolved in a small quantity of alcohol, in which the substance is readily soluble. To the hot alcoholic solution water is added until a cloudiness appears. On shaking, drops of red oil collect from which the liquid is filtered through a moistened filter. The clear filtrate on cooling deposits orange-coloured tabular crystals.

$$\underset{\text{Acetanilide}}{C_6H_5NH.C_2H_3O} + HNO_3 = \underset{\text{Nitracetanilide.}}{C_6H_4\begin{cases}NH.C_2H_3O\\NO_2\end{cases}} + H_2O$$

Properties.—Para-nitracetanilide colourless needles; m. p. 207°. On boiling a small quantity in a test-tube for a few minutes with an excess of concentrated

hydrochloric acid, until, on diluting, no precipitate is produced, the hydrochloride of para-nitraniline is formed, and on the addition of caustic potash solution the free base is precipitated in the form of acicular clusters; m. p. 147°.

Ortho-nitracetanilide orange-coloured plates; m. p. 78°. Treated with hydrochloric acid as above, it yields ortho-nitraniline, which crystallises in orange needles; m. p. 71·5°.

PREPARATION VII.

META-DINITROBENZENE, $C_6H_4O_4N_2 = C_6H_4 \begin{matrix}(1)\ NO_2 \\ (3)\ NO_2\end{matrix}$

LITERATURE.—Deville (1841), Ann. Ch. Phys. (3) 3, 187; Hofmann, Muspratt (1846), Ann. Ch. Pharm. 57, 214: Beilstein, Kurbatow (1875), Ann. Ch. Pharm. 176, 44; Rinne, Zincke (1874), Ber. 7, 869; Körner (1876), Chem. Soc. J. 14, 207.

30 grms. nitrobenzene.
35 ,, fuming nitric acid, sp. gr. 1.5.
35 ,, conc. sulphuric acid.

Thirty grms. nitrobenzene are added to a mixture of 35 grms. fuming nitric acid and 35 grms. conc. sulphuric acid contained in a flask of about half-litre capacity and well shaken after each fresh addition.* Heat is evolved, and the mass becomes somewhat deeper in colour. The

rate at which the nitrobenzene is run in is regulated by the temperature of the mixture, which should be maintained at about 70°—80°. When the nitrobenzene has been thus added, the contents of the flask are heated for a short time on the water-bath, and are poured whilst warm into a large quantity of water. The meta-dinitrobenzene, mixed with small quantities of the ortho-and para-compounds, separates out as a yellow crystalline mass, which is filtered and washed with water on the filter-pump. It is then recrystallised from hot dilute alcohol. On cooling the alcoholic solution, meta-dinitrobenzene crystallises out in colourless needles, and is free from its isomers, which remain dissolved in the mother liquor.

$$C_6H_5NO_2 + HONO_2 = C_6H_4\begin{matrix}NO_2\\NO_2\end{matrix} + H_2O$$

Nitrobenzene — Dinitrobenzene.

Properties.—Colourless long needles; m. p. 89·8°; b. p., 297°.

PREPARATION VIII.

META-NITRANILINE, $C_6H_6O_2N_2 = C_6H_4\begin{matrix}(1)\ NH_2\\(3)\ NO_2\end{matrix}$

LITERATURE.—Muspratt, Hofmann (1846), Ann. Ch. Pharm. 57, 217; Arppe (1855), Ann. Ch. Pharm. 96, 114; Beilstein, Kurbatow (1875), Ann. Ch. Pharm. 176, 44; Hübner, Frerichs (1877), Ber. 10, 1716.

50 grms. m-dinitrobenzene.
150 ,, alcohol (absolute).
25 ,, conc. ammonia.

Fifty grms. dinitrobenzene, 150 grms. alcohol (absolute), and 25 grms. conc. ammonia are mixed together in a half-litre flask, and into the dark red pasty mass sulphuretted hydrogen is passed, the mixture being well stirred meanwhile.* The dinitrobenzene slowly dissolves, and when the red liquid is saturated with the gas, crystalline flakes of ammonium thiosulphate begin to separate. When the solution is completely saturated, it is heated on the water-bath until any excess of sulphuretted hydrogen is expelled; at the same time sulphur separates out in quantity. After cooling, the liquid is again saturated with sulphuretted hydrogen as before, and heated on the water-bath, and the same process repeated until the contents of the flask have increased in weight about 30 grms. A sufficient quantity of water is now added to the liquid to precipitate the nitraniline and filtered.

In order to purify the crude product, it is repeatedly extracted with small quantities of dilute hydrochloric acid, the acid solution somewhat concentrated, whereby a small quantity of unchanged dinitrobenzene separates, and filtered. Conc. ammonia added to the filtrate precipitates the m-nitraniline, which may be purified by recrystallisation from boiling water. The filtrate from

the crude nitraniline is acidified with dilute hydrochloric acid, and evaporated to dryness on the water bath. The residue is extracted with dilute hydrochloric acid, and the filtered solution treated with conc. ammonia. In this way a further quantity of nitraniline may be obtained.

$$C_6H_4(NO_2)_2 + 3NH_4HS = C_6H_4{}^{NO_2}_{NH_2} + 3NH_3 + 3S + 3H_2O$$

Dinitrobenzene — Nitraniline.

Properties.—Yellow needles; m. p. 114°; b. p. 285°. Compare the melting point with that of ortho- and para-nitraniline, p. 28.

PREPARATION IX.

DIETHYLANILINE, $C_{10}H_{15}N = C_6H_5.N\begin{cases} C_2H_5 \\ C_2H_5. \end{cases}$

LITERATURE.—A. W. Hofmann (1850), Ann. Ch. Pharm. 74, 128.

50 grms. aniline.
65 „ ethyl bromide.

A mixture of 50 grms. pure commercial aniline and 65 grms. ethyl bromide are heated on the water-bath in a flask connected with reflux condenser. After about three hours the contents of the flask have

solidified to a brownish crystalline mass consisting of the mixed hydrobromides of diethyl-, monoethyl-aniline and aniline. Water is added, which readily dissolves the hydrobromides, and then excess of caustic potash solution. The free bases separate out as a dark brown oily layer on the surface of the liquid. The oil is carefully separated and the aqueous portion extracted with ether, the ether distilled and the residue added to the other oil. The whole is mixed with an equal weight of acetic anhydride, which causes a considerable rise of temperature and converts the aniline and monoethylaniline into the corresponding acetyl compounds, whereas the diethyl compound is unacted upon. The mixture is distilled in a retort connected with a condenser and receiver. At first excess of acetic anhydride and some acetic acid pass over. The thermometer then rises rapidly and the portion distilling above 180° is collected in a separate vessel. At this point it is advisable to run the water out of the condenser to avoid cracking the tube or to replace the condenser simply by a straight wide tube. A portion of the distillate, on cooling, solidifies to a yellow crystalline mass. The oil is drained off by filtering with the pump through a platinum cone and the residue is washed with small quantities of cold and very dilute sulphuric acid. The filtrate contains the diethylaniline. The crystalline residue consists of the acetyl compounds

of aniline and monoethylaniline.[1] The filtrate is made alkaline with caustic potash solution extracted with ether and dehydrated over solid caustic potash. The ether is distilled off on the water-bath and the residual oil fractionated over the flame. The light yellow oil passing over at 210°—215° is nearly pure diethylaniline.

$$C_6H_5NH_2 + 2C_2H_5Br = \underset{\text{Diethylaniline.}}{C_6H_5N(C_2H_5)_2} + 2HBr$$

Properties.—Colourless oil; b. p. 213·5°; sp. gr. ·936 at 18°.

PREPARATION X.

PARA-NITROSODIMETHYLANILINE,

$$C_8H_{10}N_2O = C_6H_4\overset{(1)}{\underset{(4)}{}}N(CH_3)_2\ NO.$$

LITERATURE.—Baeyer, Caro (1874), Ber. 7, 810 and 963; Schraube (1875), Ber. 8, 616; Wurster (1879), Ber. 12, 523.

[1] The monoethylaniline may be isolated by boiling the mixed acetyl compounds with slight excess of 20 per cent. hydrochloric acid for two hours, adding excess of caustic potash solution and distilling with steam. The mixture of oil and water in the receiver is acidified with dilute sulphuric acid, and a small quantity of sodium nitrite solution slowly added to the cold solution. The aniline is converted into diazobenzene sulphate, which dissolves; the ethyl aniline into ethylphenylnitrosamine, which separates as an oil and may be extracted with ether. After distilling off the ether the nitrosamine is reduced with tin and hydrochloric acid, and is reconverted into monoethylaniline (Fischer).

25 grms. dimethylaniline.
65 „ conc. hydrochloric acid diluted with 130 grms. water.
15 „ sodium nitrite.

To a solution of 25 grms. dimethylaniline in 65 grms. conc. hydrochloric acid diluted with 130 grms. water, rather more than the calculated quantity of sodium nitrite (15 grms.) dissolved in a small quantity of water is slowly added and the mixture well shaken and cooled in ice. The separation of the hydrochloride of nitrosodimethylaniline in the form of small yellow needles soon begins, and the liquid is gradually filled with a thick crystalline deposit. When after standing for some time no further increase in the quantity of crystals is observed, the mass is filtered at the pump and washed with alcohol containing hydrochloric acid. The salt may be purified by recrystallisation from hot water. It forms small yellow needles. In order to prepare the free base, the hydrochloride is mixed into a paste with water and excess of potassium carbonate or caustic soda solution added in the cold. The yellow colour of the salt changes to green and the free base, which is formed, is extracted with ether. On evaporating off the ether the base remains in the form of brilliant green foliated crystals.

$$\underset{\text{Dimethylaniline hydrochloride}}{C_6H_5N(CH_3)_2HCl} + HNO_2 = \underset{\text{p-Nitrosodimethylaniline hydrochloride.}}{C_6H_4(NO)N(CH_3)_2.HCl} + H_2O$$

Properties.—Large green foliated crystals; m. p. 85°; somewhat volatile in steam. If some of the crystals be warmed with ammonium sulphide then acidified with hydrochloric acid and ferric chloride finally added to the liquid, a deep blue coloration is produced from the formation of methylene blue (Ber. 11, 1705).

PREPARATION XI.

PARA-NITROSOPHENOL, $C_6H_5NO_2 = C_6H_4\begin{matrix}(1)O\\(4)N.OH\end{matrix}$.

(*Quinonoxime.*)

LITERATURE.—Baeyer, Caro (1874), Ber. 7, 809 and 963; Ter Meer (1875), Ber. 8, 622; Goldschmidt (1884), Ber. 17, 214.

5 grms. nitrosodimethylaniline hydrochloride.
25 „ caustic soda solution (sp. gr. 1·25.)
225 „ water.

Twenty-five grms. caustic soda solution (sp. gr. 1·25) and 225 grms. water are heated to boiling in a round-bottomed flask connected with a condenser and receiver containing dilute hydrochloric acid. Five grms. nitrosodimethylaniline are gradually added to the soda solution by removing the cork for a moment. The free base, which separates out in oily drops, is allowed to dissolve before each fresh addition. The

boiling is continued until the dark green colour of the liquid changes to reddish yellow. The greater part of the dimethylamine, formed simultaneously with the nitrosophenol, passes over with the aqueous vapour and is absorbed in the receiver.[1] The liquid in the flask is thoroughly cooled, acidified with dilute sulphuric acid and extracted with ether. On distilling off the greater part of ether from the dark green solution, the nitrosophenol remains in brown foliated crystals, which are separated from the mother-liquor and dried.

$$C_6H_4{}^{NO}_{N(CH_3)_2} + H_2O = C_6H_4{}^{NOH}_{O} + NH(CH_3)_2$$

p-Nitrosodimethylaniline — Nitrosophenol — Dimethylamine.

Properties.—Brown foliated crystals; soluble in hot water, alcohol, and ether; decomposes at 120°—130° with slight explosion leaving a residue of carbon. Dissolved in excess of phenol it gives on warming with a few drops of conc. sulphuric acid a blue solution, which changes to red on the addition of water (Liebermann's "nitroso" reaction).

[1] On evaporating down the hydrochloric acid solution on the water-bath colourless crystals of dimethylamine hydrochloride may be obtained.

PREPARATION XII.

Potassium Benzene Sulphonate, $C_6H_5.SO_3K$.

Literature.—Mitscherlich (1834), Pogg. Ann. 31, 283 and 364; Michael, Adair (1877), Ber. 10, 585.

50 grms. benzene.
100 „ conc. sulphuric acid.

Fifty grms. pure commercial benzene and 100 grms. conc. sulphuric acid are mixed together in a round-bottomed flask of about ½ litre capacity, provided with a reflex condenser, and the mixture kept at a gentle boil on the sand-bath for about twelve hours. The contents of the flask divide into two layers: The lower layer of acid assumes a dense black colour, and gradually increases in volume as the boiling continues, the upper layer of benzene diminishing in the same proportion until about four-fifths of the benzene has dissolved, when more prolonged heating produces no further change. After cooling a portion of the unattacked benzene may be separated by means of a tap-funnel. The dark-coloured acid liquid is poured into a large volume (about ½ litre) of water, and any residual benzene is driven off on the water-bath. The liquid is then neutralised whilst hot with powdered chalk mixed into a paste with water or with milk of lime. The mass is filtered hot

through cloth from the precipitate of calcium sulphate, washed with hot water, and the faintly brown coloured filtrate carefully concentrated over the flame until a sample, withdrawn on the end of a glass rod, on cooling solidifies. From the solution the calcium salt of benzene sulphonic acid separates out on cooling, and forms an almost solid mass of small, white crystals, which, after being drained from the mother-liquor, are almost pure. In order to convert the calcium salt into the corresponding potassium salt, the former is dissolved in water, and, whilst hot, a concentrated solution of potassium carbonate carefully added, until the calcium is exactly precipitated as calcium carbonate. The aqueous solution of the potassium salt is filtered from the calcium carbonate through cloth and evaporated down first over the flame and finally on the water-bath until a sample crystallises on cooling. The potassium salt crystallises in the form of colourless crystalline plates, which after filtration and thoroughly drying on unglazed earthenware (a porous plate or tile) are sufficiently pure for further treatment.

$$\underset{\text{Benzene}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzene sulphonic acid.}}{C_6H_5SO_3H} + H_2O$$

$$2C_6H_5SO_3H + CaCO_3 = \underset{\text{Calcium Benzenesulphonate.}}{(C_6H_5SO_3)_2Ca} + CO_2 + H_2O$$

$$(C_6H_5SO_3)_2Ca + K_2CO_3 = \underset{\text{Potassium Benzenesulphonate.}}{2C_6H_5SO_3K} + CaCO_3$$

Properties.—Colourless, pearly plates which slowly

effloresce in the air, and which melt above 300° with slight decomposition; very soluble in water, with difficulty in alcohol.

PREPARATION XIII.

PHENOL, $C_6H_6O = C_6H_5(OH)$.

(Carbolic acid, Oxybenzene.)

LITERATURE.—Runge (1834), Berz. Jahresb. 15, 417; Laurent (1842), Ann. Ch. Phys. (3) 3, 195; Gerhardt (1843), Ann. Ch. Pharm. 45, 25; Kekulé, Wurtz, Dusart (1867), Zeitsch. f. Ch. N. S. 3, 299, 300, 301; Degener (1878), Journ. prakt. Ch. (2), 17, 394.

20 grms. potassium benzene sulphonate
35 „ caustic potash.

Thirty-five grms. caustic potash, dissolved in the smallest quantity of water, are heated in a silver basin, preferably in the oil-bath (Fig. 15), and 20 grms. dry powdered potassium benzene sulphonate added, the mixture being well stirred.[1] The temperature of the oil-bath is maintained at 290°—295° for one hour.[2] In progress of fusion

[1] Fusions with strong potash solution under pressure in many cases give better yields. For laboratory purposes a strong steel tube, capable of resisting a high pressure, and closed by a screw plug, is used and heated in a paraffin or oil bath. The fusion requires more time and is made at a lower temperature.

[2] If no oil-bath is used, the temperature of the melt must not exceed 250°. The bulb of the thermometer should be protected by encasing it in a glass tube closed at one end.

the mass is first thick and pasty; but soon becomes semi-fluid, and remains in this condition, gradually changing in colour from yellow to brown until towards the end of the operation, when it regains somewhat its original consistency. On cooling, the melt is dissolved in water, and the alkaline reddish-brown liquid (potassium phenate and excess of alkali) acidified with conc

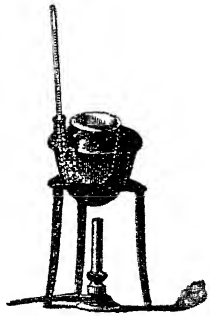


Fig. 15.

hydrochloric acid in the cold. Phenol separates out as a light yellow oil, which is extracted from the liquid with ether. The ethereal solution dehydrated over quicklime is distilled, first on the water-bath and then over the flame. The portion boiling at 175°—185° is nearly pure phenol. It distils as a colourless liquid, and solidifies at once on introducing a small crystal of the same substance.

$$\underset{\text{Potassium Benzene-sulphonate}}{C_6H_5SO_3K} + KOH = \underset{\text{Potassium Phenate.}}{C_6H_5(OK)} + KHSO_3$$

$$C_6H_5(OK) + HCl = \underset{\text{Phenol.}}{C_6H_5(OH)} + KCl$$

Properties.—Colourless needles possessing a smell resembling camphor; m. p. 40°—41°; b. p. 182°; easily soluble in water, alcohol, and ether. It is coloured violet with ferric chloride, blue with bleaching powder solution; on the addition of bromine water a yellow flocculent precipitate of tribromophenol is formed. See also Liebermann's reaction (p. 36) with nitroso-compounds and nitrites.

PREPARATION XIV.

ANISOL, $C_7H_8O = C_6H_5.OCH_3$.
(*Methyl Phenate, Phenyl Methyl Ether.*)

LITERATURE.—Cahours (1851), Ann. Ch. Pharm. 78, 226.

5 grms. sodium.
100 c.c. methyl alcohol (absolute).
20 grms. phenol.
40 ,, methyl iodide.

Five grms. sodium cut into thin slices are dissolved in 100 c.c. pure methyl alcohol contained in a flask attached to a reflux condenser. To the solution, when cool, 20 grms. phenol are added and 40 grms. methyl iodide, and without removing the condenser

the whole heated on the water-bath for several hours until the solution has no longer an alkaline reaction. A portion of the methyl alcohol and methyl iodide are distilled off on the water-bath, and water added to the amber-coloured residue. After repeatedly washing with water to dissolve out the remainder of the methyl alcohol, a colourless oil separates out, which is extracted with ether, the ethereal solution dehydrated over fused calcium chloride, and distilled first on the water-bath until the ether has been driven off and then over the flame. Almost the whole of the residue distils at 150°—155°.

$$C_6H_5OH + CH_3ONa = C_6H_5ONa + CH_3OH$$

$$\underset{\text{Sodium Phenate}}{C_6H_5ONa} + CH_3I = \underset{\text{Phenyl Methyl Ether.}}{C_6H_5OCH_3} + NaI$$

Properties.—Colourless liquid possessing an agreeable smell; b. p. 152°; sp. gr. ·991 at 15°.

PREPARATION XV.

ORTHO- AND PARA-NITROPHENOL, $C_6H_5NO_3$

$$C_6H_4\begin{matrix}(1)\ NO_2\ (1)\\(2)\ OH\ (4)\end{matrix}$$

LITERATURE.—Hofmann (1857), Ann. Ch. Pharm. 103, 347; Fritsche (1859), Ann. Ch. Pharm. 110, 150; Kekulé, Lehrbuch d. org. chem. 3, 40.

40 grms. phenol.
80 „ nitric acid, sp. gr. 1·34.
160 „ water.

To a mixture of 80 grms. nitric acid sp. gr. 1·34 and 160 grms. water, contained in a flask of about ½ litre capacity, 40 grms. melted phenol are gradually added in small quantities, and the contents of the flask well shaken. On the addition of the phenol, the liquid immediately changes to a deep brown or black colour, and a heavy dark brown oil separates out. When the whole of the phenol has been added, the mixture is allowed to stand for twelve hours. The oil has by that time collected at the bottom of the vessel, and may be freed from acid by repeatedly pouring in water, and carefully decanting. The contents of the flask consist of nearly equal quantities of para- and ortho-nitrophenol, mixed with resinous products. In order to separate the two isomers the product is distilled in a current of steam (see Fig. 12) until the distillate is almost colourless. The ortho-compound distils into the receiver in the form of a yellow oil, which solidifies at the ordinary temperature to needle-shaped crystals. By recrystallisation from hot dilute alcohol it is obtained well crystallised and pure.

The solid residue contains the para-compound mixed with black resinous substances, from which it

is separated by repeatedly extracting with boiling water. The united portions of the aqueous extract are boiled with animal charcoal and filtered. The light brown filtrate is made slightly alkaline with caustic soda solution, concentrated to a small bulk and allowed to crystallise. The brownish crystals are separated from the mother-liquor by draining and pressing at the filter-pump. These may be purified by recrystallisation from water. To obtain the free para-compound the concentrated aqueous solution of the sodium salt is acidified with dilute hydrochloric acid, and the nitrophenol, which separates out as a crystalline precipitate, is filtered and recrystallised from hot dilute alcohol.

$$\underset{\text{Phenol}}{C_6H_5(OH)} + HONO_2 = \underset{\text{Nitrophenol.}}{C_6H_4\begin{matrix}NO_2\\OH\end{matrix}} + H_2O$$

Properties. — *Ortho - nitrophenol,* sulphur - yellow needles, possessing a peculiar aromatic smell; m. p. 45°; b. p. 214°; distillable with steam; soluble in alcohol, ether, and hot water; less soluble in cold water.

Para-nitrophenol, colourless needles; m. p. 114°; easily soluble in alcohol and hot water; with difficulty soluble in cold water.

PREPARATION XVI.

PICRIC ACID, $C_6H_3N_3O_7 = C_6H_2(OH)\begin{matrix}(2)\ NO_2\\(4)\ NO_2\\(6)\ NO_2\end{matrix}$
(*α-Trinitrophenol.*)

LITERATURE.—Woulfe (1771); Dumas (1833), Ann. Ch. Phys. 53, 178, and (1841) Ann. Ch. Phys. (3), 2, 228; Laurent (1841), Ann. Ch. Phys. (3) 3, 221; Schmidt, Glutz (1869), Ber. 2, 52.

50 grms. phenol.
50 „ conc. sulphuric acid.
200 „ nitric acid, sp. gr. 1·4.

Fifty grms. commercial phenol and 50 grms. conc. sulphuric acid are heated together in a porcelain basin on the water-bath until a clear solution of phenolsulphonic acid is obtained. It is diluted with an equal volume of water, and slowly added, in small quantities at a time, from a tap-funnel, to 200 grms. nitric acid sp. gr. 1·4, contained in a flask of about ¾ litre capacity, which is well shaken during the process.* The liquid changes to a deep red colour, a considerable rise of temperature occurs, and red fumes are evolved. When the phenolsulphonic acid has been added, the flask is placed on the water-bath and heated with the addition of fuming nitric acid. On cooling, picric acid separates out as a yellow crystalline mass. It is diluted with water, filtered at the

pump and washed free from the mother-liquor with water. It is then purified by recrystallisation from hot water, acidified with a few drops of sulphuric acid.

$$\underset{\text{Phenol}}{C_6H_5(OH)} + H_2SO_4 = \underset{\text{Phenolsulphonic Acid.}}{C_6H_4{}^{OH}_{SO_3H}} + H_2O$$

$$C_6H_4{}^{OH}_{SO_3H} + 3HONO_2 = \underset{\text{Picric Acid.}}{C_6H_2(OH)(NO_2)_3} + 3H_2O + H_2SO_4$$

Properties.—Yellow prismatic crystals; m. p. 122·5°, subliming on gently heating; easily soluble in alcohol and ether; with difficulty in cold, more readily in hot water; the solution has a bitter taste. Heated gently with 2 parts of potassium cyanide in a dilute solution a brown crystalline precipitate of isopurpuric acid separates on cooling.

PREPARATION XVII.

PHENOLPHTHALEIN,

$$C_{20}H_{14}O_4 = C{}^{(C_6H_4(4)OH)_2}_{C_6H_4(2)CO.O}$$

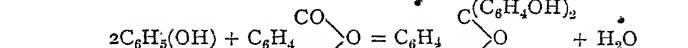
(*Di-p-oxydiphenylphthalid.*)

LITERATURE.—Baeyer (1876), Ber. 9, 1230 and (1880) Ann. Ch. Pharm. 202, 68.

10 grms. phthalic anhydride.
20 ,, phenol.
8 ,, conc. sulphuric acid.

Ten grms. phthalic anhydride, 20 grms. phenol, and 8 grms. conc. sulphuric acid are heated together to 115°—120° in the oil-bath for ten hours. The mass becomes semi-fluid and of a dark red colour. When the reaction is finished, the hot melt is poured into water, and boiled until the smell of phenol has disappeared, the water being renewed as it evaporates. The undissolved yellow granular precipitate is separated on cooling from the liquid by filtration, and washed with water. It is then dissolved in dilute caustic soda solution, filtered from the undissolved residue, and the filtrate acidified with acetic acid and a few drops of hydrochloric acid. The phthalein separates out after standing for some hours as a light yellow sandy crystalline powder. It is filtered and purified by dissolving in absolute alcohol, with the addition of animal charcoal (1 part phenolphthalein, 6 parts alcohol, and ½ part charcoal), and boiling the solution on the water-bath with a condenser for 1½ hours. The mass is filtered hot, the charcoal washed with 2 parts boiling alcohol, and the alcoholic filtrate evaporated down to two-thirds its bulk, on the water-bath. On the addition of 8 times the quantity of cold water to the cooled solution, the latter becomes turbid. The liquid is well stirred, and after standing a few seconds, filtered through cloth from the resinous oil, which separates out. On heating the filtrate for a time on the water-bath to expel excess of alcohol,

phenolphthalein crystallises out in the form of a white powder.



Phenol Phthalic Anhydride Phenolphthalein.

Properties.—White, granular, crystalline powder; m. p. 250-253°; very slightly soluble in water, readily soluble in hot alcohol; soluble in caustic alkalis with a crimson colour.

PREPARATION XVIII.

QUINONE, $C_6H_4O_2 = C_6H_4 \begin{matrix}(1)\ O \\ (4)\ O\end{matrix}$

(Benzoquinone.)

LITERATURE.—Woskresensky (1838), Ann. Ch. Pharm. 27, 268; Wöhler (1843), Ann. Ch. Pharm. 45, 354 (1850), 51, 145 (1858), 65, 349; Graebe (1868), Ann. Ch. Pharm. 146, 1; Nietzki (1882), Ann. Ch. Pharm. 215, 125 and (1886) Ber. 19, 1467.

50	grms.	aniline.
400	,,	conc. sulphuric acid.
1500	,,	water.
175	,,	potassium dichromate.[1]

Fifty grms. commercial aniline are dissolved in a mixture of 400 grms. conc. sulphuric acid and 1500

[1] An equivalent quantity of sodium dichromate dissolved in 2 to 3 times its weight of water may be used (Nietzki).

grms. water, contained in a round-bottomed flask of about 4 litres capacity, and to the well-cooled solution of aniline sulphate 175 grms. finely powdered potassium dichromate are slowly added in small portions at a time. It is necessary for the success of the operation that the flask be thoroughly well shaken after each fresh addition of dichromate, and that the temperature of the mixture does not rise above that of the outside atmosphere. Aniline black separates out at first, the greenish colour of which changes towards the end of the operation to a violet black. When all the dichromate has been added, the mixture is left for a few hours and shaken up not too vigorously two or three times with a large volume of ether. On distilling off the solvent, quinone remains in the form of yellow needle-shaped crystals, which are usually discoloured by the presence of quinhydrone. The substance is, however, sufficiently pure for most purposes, and is well adapted for the preparation of hydroquinone. By recrystallisation from ligroin the quinone is obtained well crystallised and free from quinhydrone.

The reaction consists in oxidation and elimination of the amido-group and simultaneous replacement of two hydrogen atoms in the benzene nucleus by oxygen, and cannot well be expressed in the form of equation.

Properties.—Golden yellow needle-shaped crystals; m. p. 116°; with difficulty soluble in water, readily soluble in alcohol and ether; it sublimes on heating,

and volatilises at ordinary temperatures. Its vapour has a penetrating smell, and attacks the eyes.

PREPARATION XIX.

HYDROQUINONE, $C_6H_6O_2 = C_6H_4 \begin{matrix}(1)\ OH \\ (4)\ OH\end{matrix}$
(*Paradioxybenzene*, *Paraoxyphenol*, *Quinol.*)

LITERATURE. — Pelletier, Caventou; Wöhler (1844), Ann. Ch Pharm. 51, 150; Nietzki (1882), Ann. Ch. Pharm. 215, 125.

50	grms.	aniline.
400	,,	conc. sulphuric acid.
1500	,,	water.
125	,,	potassium dichromate.

The first part of the operation in the preparation of hydroquinone is identical with that of quinone. Instead, however, of extracting with ether, the brown solution resulting from the oxidation of aniline sulphate and potassium dichromate is directly treated with either a concentrated solution of sodium bisulphite or with sulphur dioxide, the latter being passed into the liquid, until, after standing for a time, it retains the smell of the gas. The product is now repeatedly extracted with ether, the ether distilled off, and the dark-coloured residue recrystallised from water, with

the addition of sulphurous acid and animal charcoal, until it becomes colourless and gives the correct melting-point.

$$\underset{\text{Quinone}}{C_6H_4O_2} + SO_2 + 2H_2O = \underset{\text{Hydroquinone.}}{C_6H_4(OH)_2} + H_2SO_4$$

Properties.—Colourless prisms; m. p. 169°; sublimes at a gentle heat; easily soluble in alcohol, ether, and hot water, less soluble in cold water.

PREPARATION XX.

BENZYL CHLORIDE, $C_7H_7Cl = C_6H_5CH_2Cl$.

LITERATURE.—Cannizzaro (1853), Ann. Ch. Pharm. 88, 129; and (1855) 96, 246; Beilstein, Geitner (1866), Ann. Ch. Pharm. 139, 331.

100 grms. toluene.

One hundred grms. toluene (b. p. 110—111°) are gently boiled in a tared retort of about 300 c.c. capacity to which a reflux condenser is connected, and into the boiling liquid dry chlorine is conducted[1] in a somewhat rapid stream, preferably in direct sunlight (Fig. 16).* The process is continued until the retort has gained 37 grms. in weight. The liquid becomes light yellow

[1] The chlorine is evolved by gently warming a mixture of manganese dioxide in lumps and conc. hydrochloric acid. The gas is dried through strong sulphuric acid.

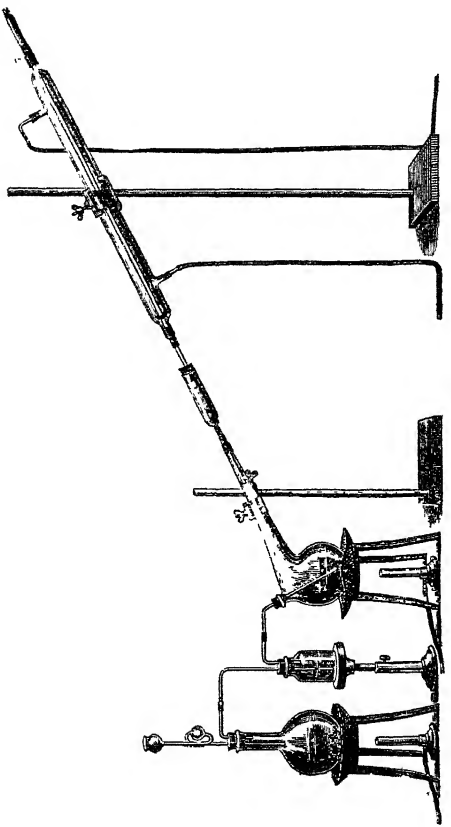


FIG. 16

in colour and hydrochloric acid fumes are evolved at the upper end of the condenser. When the reaction is complete, the contents of the retort are distilled.* At first unchanged toluene distils; the fraction boiling at 165—185° contains nearly the whole of the benzyl chloride, and forms the greater part of the product. The liquid which passes over above 185° is a mixture of higher chlorinated compounds, and consists chiefly of benzylene and benzenyl-chlorides. The portion containing the benzyl chloride is repeatedly fractionated until a liquid is obtained boiling at 176—180°, which is nearly pure benzyl chloride.

$$\underset{\text{Toluene}}{C_6H_5CH_3} + 2Cl = \underset{\text{Benzyl Chloride.}}{C_6H_5CH_2Cl} + HCl$$

Properties.—Colourless liquid with a penetrating smell; b. p. 179°; sp. gr. 1·107 at 14°.

PREPARATION XXI.

BENZALDEHYDE, $C_7H_6O. = C_6H_5COH.$
(*Bitter Almond Oil.*)

LITERATURE.—Liebig, Wöhler (1837), Ann. Ch. Pharm. 22, 1; Lauth, Grimaux (1867), Ann. Ch. Pharm. 143, 186.

50 grms. benzyl chloride.
40 ,, copper nitrate.
500 ,, water.

Fifty grms. benzyl chloride and 40 grms. copper nitrate, dissolved in 500 grms. water are heated to boiling in a round-bottomed flask with reflux condenser on the sand-bath for 8 to 10 hours. A slow current of carbonic acid is at the same time passed through the liquid to prevent oxidation of the benzaldehyde by absorption of oxygen from the air. During the process nitrous fumes are slowly evolved. When the reaction is complete the contents of the flask are extracted with ether, and the yellowish oil remaining, after distilling off the ether, is well shaken with a saturated solution of sodium bisulphite,[1] and allowed to stand for a time. The colourless crystalline mass which separates out is filtered, washed with alcohol and ether and then drained on the filter. The aldehyde is regained from the sodium bisulphite compound by heating with excess of sodium carbonate solution or dilute sulphuric acid, and distilled over with steam. The distillate is extracted with ether, and the residue left after distilling off the ether is dehydrated over calcium chloride. The benzaldehyde is redistilled and is then pure.

$$\underset{\text{Benzyl Chloride}}{2C_6H_5.CH_2Cl} + Cu(NO_3)_2 = \underset{\text{Benzaldehyde.}}{2C_6H_5COH} + CuCl_2 + 2HNO_2$$

[1] The solution is prepared by passing sulphur dioxide into powdered sodium carbonate covered with a layer of water. The carbonate dissolves with effervescence, forming a heavy apple-green liquid smelling strongly of sulphur dioxide.

Properties.—Colourless liquid, with a pleasant aromatic smell; b. p. 179°; sp. gr. 1·0504 at 15°; it quickly oxidises in the air, forming benzoic acid; in contact with strong aqueous ammonia, crystals of hydrobenzamide are deposited. Add to a drop of the aldehyde in half a test-tube full of water a solution of 1 pt. phenylhydrazine hydrochloride, 1½ pts. sodium acetate, and 8—10 pts. water. On shaking a thick white flocculent precipitate is formed (Fischer's reaction for aldehydes, Ber. 17, 574).

PREPARATION XXII.

BENZYL ALCOHOL, $C_7H_8O = C_6H_5CH_2OH$.

LITERATURE.—Cannizzaro (1853), Ann. Ch. Pharm. 88, 129; and (1855) Ann. Ch. Pharm. 96, 216; R. Meyer (1881), Ber. 14, 2394.

40 grms. benzaldehyde.
36 „ caustic potash.
24 „ water.

Forty grms. benzaldehyde, and a solution of 36 grms. caustic potash in 24 grms. water are shaken together in a well-stoppered bottle until a permanent emulsion is formed. The contents of the bottle after a short time become hot, and on standing for about twenty hours, solidify to a mass of white crystals of potassium

benzoate. Water is added (about 200 c.c.) sufficient to dissolve the crystals, the benzyl alcohol also going into solution. The clear solution is extracted repeatedly with ether, the ether expelled and the colourless residual oil directly distilled without being previously dehydrated. As soon as the last traces of ether have passed over, the thermometer rises rapidly to the boiling point of benzyl alcohol and the whole distils within 2 to 3 degrees.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + KOH = \underset{\text{Benzyl Alcohol}}{C_6H_5CH_2(OH)} + \underset{\text{Potassium Benzoate.}}{C_6H_5COOK}$$

Properties.—Colourless liquid with a faint aromatic smell; b. p. 206·5°; sp. gr. 1·0507 at 15·4°.

PREPARATION XXIII.

α-Toluic Acid, $C_8H_8O_2 = C_6H_5CH_2CO_2H$. (*Phenylacetic Acid*).

Literature.—Cannizzaro (1855), Ann. Ch. Pharm. 96, 247; T. Maxwell (1879), Ber. 12, 1764; Spiegel (1881), Ber. 14, 239; Mann (1881), Ber. 14, 1645; Staedel (1886), Ber. 19, 1951.

60 grms potassium cyanide (pure).
55 ,, water.
100 ,, benzyl chloride.
100 ,, alcohol.

In a $\frac{3}{4}$ litre round-bottomed flask, to which a reflux condenser is attached, 60 grms. pure potassium cyanide are dissolved in 55 grms. water. A solution of 100 grms. benzylchloride in 100 grms. alcohol are poured slowly into the hot solution of potassium cyanide through the top of the condenser. The whole is then gently boiled for 3–4 hours on the sand-bath.* The liquid separates into two layers, and as the boiling continues the upper layer gradually assumes a brown colour, and at the same time crystals of potassium chloride separate out at the bottom of the vessel. At the end of this time the flask is allowed to cool, and the upper dark brown liquid, consisting of an alcoholic solution of benzyl cyanide, decanted from the crystalline deposit of potassium chloride and distilled over wire gauze.* The thermometer stands for some time at about 80° until the alcohol is all off, a small quantity of water and benzyl cyanide distil at 100°; the temperature then rises quickly to 210°, and the fraction boiling at 210—235° consisting chiefly of benzyl cyanide is collected apart. It has a slightly brownish yellow colour. By the action of sulphuric acid it is converted into phenylacetic acid.

50 grms. benzylcyanide.

150 „ sulphuric acid { 3 vol. conc. sulphuric acid. / 2 „ water.

50 grms. benzyl cyanide and 150 grms. of a mixture of 3 vol. conc. sulphuric acid and 2 vol. water are introduced into a ½ litre flask, which is connected by a glass tube bent twice at right angles with a Woulff bottle. The end of this tube passes just beneath the cork in the one tubulus of the bottle which contains water. Through the second tubulus a vertical glass tube about 1½ foot long is fitted and dips just below the surface of the water. About the middle of the tube a large bulb is blown. The flask containing the mixture (which divides into two layers) is heated over the naked flame gently at first, and then the temperature gradually raised until small bubbles of gas are observed to rise from the surface of the lower layer of acid. The flame is now removed, and in a few minutes a strong reaction begins; the liquid boils and a small quantity of benzyl cyanide distils over into the Woulff bottle. At the same time the water is forced up the vertical tube into the bulb, which serves as a valve. The reaction is over in about half a minute; the flask is again heated for 2-3 minutes and then allowed to cool. On standing the liquid solidifies to a laminated crystalline mass. It is purified by washing with cold water. The crystals are dissolved in water, neutralised with sodium carbonate solution, the hot solution filtered and acidified with dilute sulphuric acid. On standing, colourless plates of the free acid separate which are filtered and washed. These may be

further purified by a second crystallisation from hot water.

$$\underset{\text{Benzyl Chloride}}{C_6H_5CH_2Cl} + KCN = \underset{\text{Benzyl Cyanide.}}{C_6H_5CH_2CN} + KCl$$

$$2C_6H_5CH_2CN + 4H_2O + H_2SO_4 = \underset{\text{a-Toluic Acid.}}{2C_6H_5CH_2COOH} + (NH_4)_2SO_4$$

Properties.—Colourless, thin laminated crystals; m. p. 76·5°; b. p. 262°.

PREPARATION XXIV.

SALICYLALDEHYDE (Ortho-oxybenzaldehyde).—PARA-OXYBENZALDEHYDE.

$$C_7H_6O_2 = C_6H_4 \begin{matrix}(1)\ OH \quad (1).\\ (2)\ CHO\ (4).\end{matrix}$$

LITERATURE.—Reimer, Tiemann (1876), Ber. 9, 824; Tiemann, Herzfeld (1877), Ber. 10, 62 and 213

50	grms.	phenol.
100	,,	caustic soda.
160	,,	water.
75	,,	chloroform.

Fifty grms. phenol are dissolved in a solution of caustic soda containing 100 grms. caustic soda in 160 grms. water, and the whole introduced into a 1 litre round-bottomed flask provided with a reflux condenser, and then heated to 50—60°. 75 grms. chloroform

are slowly added through the condenser, and after each addition the flask is well shaken. A gentle reaction sets in and the temperature rises. At the same time the surface of the brownish yellow solution takes a violet red tint, which rapidly fades, the liquid finally assuming a deep red colour. When the whole of the chloroform has been added the contents of the flask are boiled for ½ hour without removing the condenser, and a yellow semi-solid mass separates out of the solution. The unattacked chloroform is now distilled off on the water-bath, the liquid diluted with water and strongly acidified with dilute hydrochloric or sulphuric acid. A thick dark red oil separates out on the surface, which is subjected to distillation in steam. An oil having a faintly yellow colour distils over with the water and settles to the bottom of the receiver. When drops of oil cease to condense, the distillation is stopped. The distillate, which contains salicyl-aldehyde and phenol, is extracted with ether and the ethereal solution well shaken with a saturated solution of sodium bisulphite. The bisulphite compound of salicylaldehyde separates out in colourless needles, which are filtered, washed free from traces of phenol with alcohol and then decomposed by heating with dilute sulphuric acid. The aldehyde which separates out is taken up with ether and the ether driven off. It is dehydrated over calcium chloride and finally distilled. In the distilling flask from which the salicyl

aldehyde has in the first instance been removed with steam, there remains a brownish liquid and a dark red substance, which sinks to the bottom of the vessel and forms a brittle resin on cooling. The aqueous portion is filtered hot through a moistened filter, which retains the resin, and the filtrate containing p-oxybenzaldehyde formed simultaneously in the above reaction is extracted when cold with ether. On distilling off the solvent, p-oxybenzaldehyde remains in the form of a yellow mass of stellar-shaped needles, which may be purified by recrystallisation from small quantities of hot water.

$$C_6H_5ONa + 3NaOH + CHCl_3 = C_6H_4\begin{matrix}ONa\\CHO\end{matrix} + 3NaCl + 2H_2O$$

Sodium Phenate — Chloroform — Sodium p-Oxybenzaldehyde

Properties—Salicylaldehyde. Colourless pleasant-smelling oil, b. p. 196·5°; sp. gr. 1·1731 at 13·5°; solidifies at −20° in large crystals. Volatile in steam; soluble in water; miscible in all proportions with alcohol and ether. The aqueous solution is coloured deep violet with ferric chloride.

Paraoxybenzaldehyde. Colourless needles; m. p. 115—116°; with difficulty soluble in cold water, more readily soluble in hot water, alcohol, and ether. Not volatile in steam. The bisulphite of sodium compound is easily soluble in water. Ferric chloride colours the aqueous solution violet

PREPARATION XXV.

ACETOPHENONE, $C_8H_8O = C_6H_5.CO.CH_3$.
(*Phenylmethylketone.*)

LITERATURE.—Friedel (1858), Compt. rend. 47, 552.

100 grms. calcium benzoate.[1]
50 „ calcium acetate.

One hundred grms. finely powdered and anhydrous calcium benzoate are thoroughly mixed with 50 grms. dry powdered calcium acetate. An iron tube is half filled with the mixture. The tube is placed in a furnace, connected with condensing tube and receiver (Fig. 17), and rapidly heated from the open end towards the closed end until no more liquid condenses. A brown oil distils over. The distillate, which contains a little water, is dehydrated over calcium chloride and fractionated. A small quantity of a colourless low-boiling liquid containing benzene first distils, the temperature then rises quickly to

[1] *Preparation of Calcium Benzoate and Acetate.*—A hot solution of 100 grms. benzoic acid in about 1 litre water is made alkaline with milk of lime, filtered from excess of lime and concentrated. The hydrated lime salt crystallises on cooling in long needles, which are separated from mother-liquor, dried at 100°, finely powdered, and then freed from water by heating the salt on a flat iron tray with constant stirring until moisture ceases to condense on the cold surface of a watch-glass held above the substance. Calcium acetate is prepared similarly.

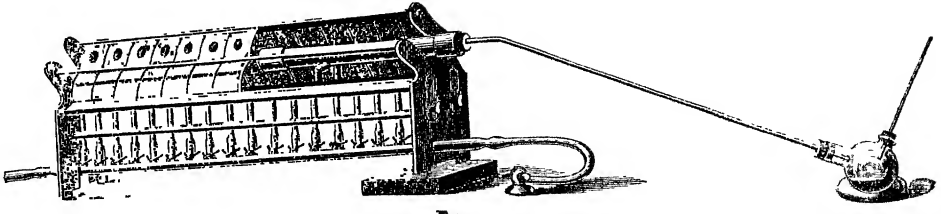


FIG. 17.

195°, and the product boiling at 195—205° and possessing a faint yellow colour is separately collected. This portion is fractionated between 198° and 202° and is nearly pure acetophenone. It crystallises on cooling to 0°.

$$\underset{\text{Calcium Benzoate}}{(C_6H_5COO)_2Ca} + \underset{\text{Calcium Acetate}}{(CH_3COO)_2Ca} = 2\underset{\text{Acetophenone.}}{C_6H_5COCH_3} + 2CaCO_3$$

Properties.—Colourless tabular crystals; b. p. 202°; m. p. 20·5°.

PREPARATION XXVI.

BENZOIN, $C_{14}H_{12}O_2 = \begin{matrix} C_6H_5CH(OH). \\ C_6H_5\dot{C}O. \end{matrix}$

(*Oxybenzylphenylketone.*)

LITERATURE.—Liebig, Wöhler (1832), Ann. Ch. Pharm. 3, 276; Zinin (1840), Ann. Ch. Pharm. 34, 186; Zincke (1879), Ann. Ch. Pharm. 198, 151.

50 grms. benzaldehyde.
5 „ potassium cyanide.
200 „ alcohol 50 per cent.

Fifty grms. benzaldehyde are added to a solution of 5 grms. commercial potassium cyanide in 200 grms. alcohol 50 per cent., and the mixture is heated on the

water-bath with a condenser for about half an hour. On cooling the liquid, benzoin separates out as a mass of small colourless crystals, which are filtered off from the mother liquor. From the latter a further quantity of benzoin may be obtained by adding 2—3 grms. potassium cyanide and again heating for a short time on the water-bath. The second crop of crystals is added to the first and the whole recrystallised from hot alcohol.

$$\underset{\text{Benzaldehyde}}{2C_6H_5COH} = \underset{\text{Benzoin.}}{\begin{matrix} C_6H_5CO \\ C_6H_5\dot{C}HOH \end{matrix}}$$

Properties.—Colourless prisms; m. p. 137°; with difficulty soluble in water; easily soluble in alcohol and ether. The solution in dilute alcohol reduces Fehling's solution on warming. On oxidation with nitric acid it yields benzil, $C_6H_5CO{\cdot}CO{\cdot}C_6H_5$.

Benzil.—15 grms. benzoin.
35 „ conc. nitric acid sp. gr. 1·4.

Fifteen grms. benzoin are heated on the water-bath with 35 grms. conc. nitric acid in a flask connected with an air condenser, the flask being well shaken. Nitrous fumes are evolved and the crystals of benzoin are converted into a yellow oil, which after two hours heating is free from unchanged benzoin. After oxidation the contents of the flask are poured into water and the yellow crystalline deposit separated by filtra-

tion, washed with water and recrystallised from alcohol or ether.

$$\begin{matrix} C_6H_5CO \\ C_6H_5\dot{C}HOH \end{matrix} + O = \begin{matrix} C_6H_5CO \\ C_6H_5\dot{C}O \end{matrix} + H_2O.$$

Properties.—Yellow prisms; m. p. 95°; insoluble in water, easily soluble in hot alcohol and ether; dissolves in cold alcoholic potash solution with a violet colour.

PREPARATION XXVII.

BENZILIC ACID, $C_{14}H_{12}O_3 = (C_6H_5)_2C(OH)\cdot CO_2H$. (*Diphenylglycollic Acid.*)

LITERATURE.—Liebig (1838), Ann. Ch. Pharm. 25, 25; Zinin (1839), Ann. Ch. Pharm. 31, 329; E. Fischer (1880), Ber. 14, 326.

10 grms. benzil.
50 „ caustic potash.

Fifty grms. caustic potash are melted with a small quantity of water in a silver crucible on the oil-bath. The temperature of the mass is brought to 150° and 10 grms. finely powdered dry benzil added. The benzil melts and the contents of the crucible shortly change to a solid mass of potassium benzilate. The cooled melt is dissolved in water and the alkaline

solution acidified with hydrochloric acid, which precipitates the benzilic acid.

The crystalline mass, which contains small quantities of benzoic acid, is separated from the mother-liquor and washed with cold water. It is then transferred to a porcelain basin, dissolved in hot water and the solution boiled until the smell of benzoic acid has entirely disappeared. On cooling, benzilic acid crystallises out and is purified by a second crystallisation from hot water.

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + KOH = (C_6H_5)_2COH.COOK$$

Benzil — Potassium Benzilate.

Properties.—Colourless needles; m. p. 150°; scarcely soluble in cold, readily in hot water and alcohol; dissolves in conc. sulphuric acid with an intense red colour.

PREPARATION XXVIII.

BENZOYL CHLORIDE, $C_7H_5OCl = C_6H_5COCl$.

LITERATURE.—Wöhler (1832) Ann. Ch. Pharm. 3, 262; Cahours (1846), Ann. Ch. Pharm. 60, 255, and (1849), 70, 40.

50 grms. benzoic acid.
30 ,, phosphorus trichloride.[1]

[1] The pentachloride may also be used, in which case three times the quantity must be taken. The reaction is started by

Fifty grms. dry benzoic acid are introduced into a flask connected with a condenser and 30 grms. phosphorus trichloride are added.* When the reaction which proceeds at the ordinary temperature is finished, the contents of the flask are heated on the oil-bath to 120° until the evolution of hydrochloric acid ceases. The benzoyl chloride is obtained from the liquid product by distillation. Unchanged phosphorus trichloride first passes over, the thermometer then rises to 195° and benzoyl chloride begins to distil. The latter after a second distillation is chemically pure.

$$\underset{\text{Benzoic Acid}}{3C_6H_5CO_2H} + PCl_3 = \underset{\text{Benzoyl Chloride.}}{3C_6H_5COCl} + P(OH)_3$$

Properties.—Colourless liquid with a penetrating odour; b. p. 198·5°; sp. gr. 1·2142 at 19°; decomposes with water forming hydrochloric acid and benzoic acid. With ammonia it yields benzamide ($C_6H_5CONH_2$).

Benzamide.—5 grms. benzoyl chloride.
10 „ ammonium carbonate.

Five grms. benzoyl chloride are slowly added to 10 grms. finely powdered commercial ammonium carbonate and thoroughly mixed in a mortar.* The reaction proceeds quietly. If the smell of benzoyl

warming, and is complete when the benzoic acid has dis olved. Hydrochloric acid is evolved, and phosphorus oxychloride formed, the latter being removed by fractional distillation.

chloride does not entirely disappear, the mass is heated for about twenty minutes on the water-bath or a few drops of strong aqueous ammonia added. It is allowed to cool, extracted with cold water and filtered. The benzamide remains on the filter in the form of a white crystalline powder, and may be recrystallised from a small quantity of boiling water.

$$\underset{\text{Benzoyl Chloride}}{C_6H_5COCl} + 2NH_3 = \underset{\text{Benzamide.}}{C_6H_5CONH_2} + NH_4Cl$$

Properties.—Colourless plates; m. p. 128°; b. p. 290°; scarcely soluble in cold, more readily in boiling water; soluble in alcohol and ether.

PREPARATION XXIX.

SULPHOCARBANILIDE, $C_{13}H_{12}N_2S = CS\overset{NHC_6H_5}{\underset{NHC_6H_5}{}}$.

(*Diphenylthiourea, Thiocarbanilide.*)

LITERATURE.—Hofmann (1849), Ann. Ch. Pharm. 70, 142; Weith (1873), Ber. 6, 967; Losanitsch (1886), Ber. 19, 1821.

100 grms. aniline
50 „ carbon bisulphide
50 „ absolute alcohol.

A solution of 100 grms. pure commercial aniline, 50 grms. carbon bisulphide,[1] and 50 grms. absolute

[1] Carbon bisulphide being very volatile and exceedingly inflammable, great care must be taken when using this substance in the neighbourhood of a flame.

alcohol, are heated for about twenty-four hours on the water-bath in a round-bottomed flask connected with a reflux condenser.* The contents of the flask, on cooling, solidify to a mass of crystalline plates. After distilling off the unattacked carbon bisulphide on the steam-bath, the residue is washed repeatedly with small quantities of very dilute hydrochloric acid in order to dissolve any unchanged aniline, and the filtered and well-pressed crystals are re-crystallised from hot dilute alcohol. On cooling, thiocarbanilide separates in colourless plates.

$$\underset{\text{Aniline}}{2C_6H_5NH_2} + CS_2 = \underset{\text{Sulphocarbanilide.}}{CS\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}} + H_2S$$

Properties. — Colourless rhombic plates; m. p. 151°; scarcely soluble in water; easily soluble in alcohol and ether.

PREPARATION XXX.

PHENYL THIOCARBIMIDE, $C_7H_5NS = CSNC_6H_5$.
(*Phenyl Mustard Oil.*)

LITERATURE.—Hofmann (1858), Jahresb. 349; Weith, Merz (1869), Zeitschr. 589.

50 grms. Sulphocarbanilide.

Fifty grms. sulphocarbanilide are boiled with two to three times the quantity of conc. hydrochloric acid in

a flask connected with a reflux condenser for about half an hour. The diphenylthiourea is decomposed into triphenylguanidine, which remains as the hydrochloride salt in solution, and phenyl mustard oil, which separates out as a brown oil. On distilling the product with steam, phenyl mustard oil collects at the bottom of the receiver as an almost colourless oil, and is separated from the aqueous layer either by extracting with ether or by means of a tap-funnel. It is dehydrated over calcium chloride, and finally distilled over a small quantity of phosphorus pentoxide.

$$2CS\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix} + HCl = CSNC_6H_5 + C\begin{matrix}.NHC_6H_5\\:NC_6H_5\end{matrix}NHC_6H_5HCl + H_2S$$

Sulphocarbanilide — Phenyl Mustard Oil — Triphenylguanidine Hydrochloride.

Properties.—Colourless oil; b. p. 220°; sp. gr. 1·135 at 15°; insoluble in water; soluble in alcohol; on heating with alcoholic ammonia (1 vol. phenyl mustard oil, 1 vol. alcohol, 3 vols. conc. ammonia) it is converted into sulphocarbanilamide, $NH_2.CS.NH(C_6H_5)$, which, on cooling, crystallises out in colourless needles.

Triphenylguanidine. — In order to separate the triphenylguanidine remaining in the flask as hydrochloride after distilling off the phenyl mustard oil, the hot solution is filtered and somewhat concentrated. The colourless salt, which crystallises out on cooling, is washed with a small quantity of water, and warmed

gently with dilute caustic soda solution. The base is set free as a white powder. It is washed with water and purified by re-crystallising from alcohol, with the addition, if necessary, of animal charcoal. Colourless needles; m. p. 143°.

PREPARATION XXXI.

BENZONITRIL, $C_7H_5N = C_6H_5CN$.

LITERATURE.—Letts (1872), Ber. 5, 669; Sandmeyer (1884), Ber. 17, 2653; Krüss (1884), Ber. 17, 1767.

50 grms. benzoic acid
19 „ potassium sulphocyanide.

A mixture of 50 grms. dry benzoic acid and 19 grms. dry potassium sulphocyanide are heated in a retort of half litre capacity connected with an air condenser on the oil-bath or over the bare flame.* The mixture melts and forms two layers, of which the lower one is benzoic acid. At 190° the reaction commences, sulphuretted hydrogen and carbonic acid being evolved; at a higher temperature the liquid begins to boil and soon swells up and solidifies to a white mass. The contents of the retort are now directly distilled from the same vessel, and the distillation continued until no more liquid passes over, care being taken not to char the residue in the retort

which consists of potassium benzoate. Dilute ammonia is added to the semi-solid distillate containing benzonitril and benzoic acid, and the liquid extracted with ether. On evaporating off the ether benzonitril remains as an oily liquid and is purified by distillation.

$$\underset{\text{Benzoic Acid}}{2C_6H_5CO_2H} + KCNS = \underset{\text{Benzonitril.}}{C_6H_5CN} + C_6H_5CO_2K + CO_2 + H_2S$$

Properties.—Colourless liquid smelling slightly of bitter almonds; b. p. 191°; sp. gr. 1·023 at 0°.

PREPARATION XXXII.

DIAZOBENZENE NITRATE, $C_6H_5O_3N_3 = C_6H_5N : N.O.NO_2$.

LITERATURE.—Griess (1866), Ann. Ch. Pharm. 137, 39; Sandmeyer (1884), Ber. 17, 2653; Klason (1887), Ber. 20, 349.

15 grms. aniline.
16 „ nitric acid sp. gr. 1·4.

Fifteen grms. pure commercial aniline are dissolved in the cold in the calculated quantity of nitric acid sp. gr. 1·4 (16 grms.) previously diluted with 20 c.c. water, and the crystalline mass filtered and washed with small quantities of cold water until free from mother-liquor. The crystals of aniline nitrate are rubbed with a little water into a stiff paste, and a fairly rapid current of

nitrogen trioxide[1] passed into the mixture, which is kept well cooled with ice* (Fig. 18). Special care must be taken that the temperature of the liquid does not exceed 10° during the operation. After fifteen to twenty minutes the crystals have dissolved and the reaction is then complete. Alcohol (about three times the volume of (absolute) alcohol) is added to the resulting dark-coloured fluid, whereby a crystalline magma of fine needles separates, the quantity of which

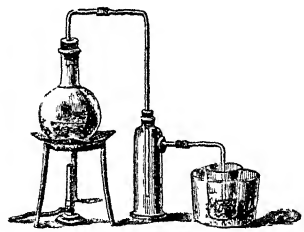


FIG 18.

further increases on the addition of ether. The crystalline precipitate is filtered (with funnel and platinum cone only) and washed free from the mother liquor with a mixture of alcohol and ether. The crystals must be kept moist, as in the dry state a

[1] Nitrogen trioxide is prepared from small pieces of arsenic trioxide, which are placed in a flask and covered with a layer of conc. nitric acid. On gently warming, nitrogen trioxide is evolved, and is freed from any nitric acid which may be carried over by passing it through an empty vessel (Fig. 18).

slight touch may produce a violent explosion. The salt, when colourless, is therefore immediately subjected to further treatment, as described below.

$$\underset{\text{Aniline Nitrate}}{C_6H_5NH_2.HNO_3} + HONO = \underset{\text{Diazobenzene Nitrate.}}{C_6H_5N:N.ONO_2} + H_2O$$

Properties.—Colourless capillary needles; easily soluble in water; with difficulty soluble in alcohol; insoluble in ether.

Iodobenzene.—Three-quarters of the diazobenzene nitrate prepared as above is dissolved in water, and aqueous hydriodic acid or a strong aqueous solution of potassium iodide slowly added. The diazo-compound is rapidly decomposed with an abundant evolution of nitrogen and the iodobenzene separates from the aqueous solution as a heavy oil. When on further addition of potassium iodide no more oil forms, the contents of the vessel are distilled with steam, and the iodobenzene, which collects in the receiver, purified as in the case of bromobenzene. (Colourless liquid, which soon turns red on standing; b. p. 188°; sp. gr. 1·69). A portion of the remaining diazo-compound is warmed in a test-tube with water. When the evolution of nitrogen has ceased, the smell of phenol will be apparent. On treating another portion in the same way with alcohol, benzene is formed. If to a fourth portion, dissolved in water, a little bromine dissolved in potassium bromide be

added a brown oil separates out, which, on pouring off the water and adding ether, solidifies. This is diazobenzene perbromide. On boiling with alcohol bromobenzene is formed. Not more than half a grm. of the substance is dried on filter-paper. On being struck or heated it detonates.

PREPARATION XXXIII.

DIAZOAMIDOBENZENE, $C_{12}H_{11}N_3 = C_6H_5N : N.NHC_6H_5$

LITERATURE.—Griess (1862) Ann. Ch. Pharm. 121, 258 and (1866) Ann. Ch. Pharm. 137, 53; Martius (1866), Zeitschr. f. Ch. N. S. 2, 381; Staedel, Bauer (1886), Ber. 19, 1952.

20 grms. aniline
6 ,, conc. sulphuric acid
600 ,, water
7·4 ,, sodium nitrite.

Six grms. conc. sulphuric acid diluted with 600 grms. water are added to 20 grms. aniline contained in a beaker of about $1\frac{1}{2}$ litre capacity. About half the aniline dissolves as sulphate. The liquid is heated to 27° and maintained at a temperature of 27° to 30° for fifteen minutes, 7·4 grms. commercial sodium nitrite dissolved in a small quantity of water being meanwhile slowly added, and the whole well stirred.

If the temperature falls below 25° or rises above 35° an impure product is obtained. As soon as the sodium nitrite is added the liquid turns yellow, and rapidly becomes turbid from the formation of diazoamidobenzene, which separates out as a yellowish brown crystalline precipitate. The solution is now allowed to stand at the ordinary temperature for half an hour, when almost the whole of the diazoamidobenzene crystallises out. It is filtered, washed with cold water, pressed well on the filter, and dried between filter paper. It forms a sandy powder, and may be purified by re-crystallisation from benzene or alcohol. For the preparation of amidoazobenzene the dry powder is sufficiently pure.

$$\underset{\text{Aniline Sulphate}}{(C_6H_5NH_2)_2H_2SO_4} + 2NaNO_2 + 2H_2SO_4 = \underset{\text{Diazobenzene Sulphate.}}{2C_6H_5N : N.OSO_3H} + Na_2SO_4 + 4H_2O$$

$$2C_6H_5N : N.OSO_3H + 2C_6H_5NH_2 = \underset{\text{Diazoamidobenzene}}{2C_6H_5N{:}N.NHC_6H_5} + 2H_2SO_4$$

N.B.—The sulphuric acid set free in the second phase of the reaction acts upon the sodium nitrite, so that one molecule only is required.

Properties.—Golden yellow plates (from alcohol); m. p. 91°; insoluble in water; difficultly soluble in cold alcohol; more readily soluble in hot alcohol, ether, and benzene; it explodes when heated above its melting point.

PREPARATION XXXIV.

AMIDOAZOBENZENE, $C_{12}H_{11}N_3 = C_6H_5N : NC_6H_4NH_2$.
(*Aniline yellow.*)

LITERATURE.—Mène (1861), Jahresb. 496; Kekulé (1866), Zeitsch. f. Ch. N. F. 2, 689; Staedel, Bauer (1886), Ber. 19, 1953.

10 grms. diazoamidobenzene.
25 ,, aniline.
5 ,, aniline hydrochloride.

Ten grms. diazoamidobenzene, 25 grms. aniline and 5 grms. powdered aniline hydrochloride are mixed together at the ordinary temperature, and the mixture then heated to 40°—50°, and maintained at this temperature for an hour. The mixture forms a clear deep red solution. After standing for twenty-four hours at the ordinary temperature, the diazoamidobenzene is converted into amidoazobenzene. An excess of conc. hydrochloric acid is added, care being taken that no great evolution of heat occurs. (If unchanged diazoamidobenzene is present, there is evolution of nitrogen with effervescence.) On cooling, the amidoazobenzene separates out together with aniline hydrochloride, as a thick crystalline mass. This is filtered and washed with dilute hydrochloric acid and water, when small violet crystals of amidoazobenzene hydrochloride remain on the filter. The salt is dissolved in boiling

water, with the addition of a small quantity of dilute hydrochloric acid, and crystallises on cooling in steel-blue needles. In order to prepare the free base, the hydrochloride is heated with rather more than double the weight of alcohol, and conc. ammonia slowly added, until the colour of the solution changes to light brown. On the gradual addition of water the base crystallises out in brown needles, which may be purified by a second crystallisation from dilute alcohol with the addition of animal charcoal.

$$\underset{\text{Diazoamidobenzene}}{C_6H_5N:N.NHC_6H_5} = \underset{\text{Amidoazobenzene.}}{C_6H_5N:N.C_6H_4NH_2}$$

Properties.—Yellow rhombic prisms; m. p. 123°; b. p. above 300°. Scarcely soluble in hot water, more readily in hot alcohol.

PREPARATION XXXV.

PHENYLHYDRAZINE, $C_6H_8N_2=C_6H_5NH.NH_2$.

LITERATURE.—E. Fischer (1878), Ann. Ch. Pharm. 190, 167; Meyer, Lecco (1883), Ber. 16, 2976.

20 grms. aniline.
400 ,, conc. hydrochloric acid.
15 ,, sodium nitrite.
90 ,, stannous chloride.

Twenty grms. pure commercial aniline are dissolved in 400 grms. conc. hydrochloric acid, and the resulting

solution of aniline hydrochloride well cooled in ice, and 15 grms. sodium nitrite dissolved in about 100 c.c. water added, the temperature of the mixture being kept at 0°. Diazobenzene chloride is formed, and the solution becomes cloudy from the separation of sodium chloride. To the mixture, which is still cooled in ice, 90 grms. commercial stannous chloride dissolved in about an equal weight of conc. hydrochloric acid are added. A thick white crystalline precipitate of phenylhydrazine hydrochloride almost immediately forms, and is separated from the mother-liquor by filtration. The free base is obtained by decomposing the hydrochloride with caustic soda. The former is therefore dissolved in a small quantity of hot water, an excess of caustic soda solution added and the mixture well shaken. The free base, which separates as a reddish-coloured oil, is extracted with ether, and the oily liquor, left on distilling off the ether, is dehydrated over anhydrous potassium carbonate and rectified.

$$\underset{\text{Aniline Hydrochloride}}{C_6H_5NH_2.HCl} + NaNO_2 + HCl = \underset{\text{Diazobenzenechloride.}}{C_6H_5N : N.Cl} + NaCl + 2H_2O$$

$$C_6H_5N : N.Cl + SnCl_2 + HCl = \underset{\text{Phenylhydrazine,}}{C_6H_5NH.NH_2} + SnCl_4$$

Properties.—Faint yellow-coloured oil, which solidifies in the cold to tabular crystals; m. p. 23°; b. p. 233—234°; sp. gr. 1·091 at 21°; scarcely soluble in cold water, more readily in hot water; almost inso-

luble in concentrated solutions of the alkalies ; easily soluble in alcohol, ether, and benzene. Phenylhydrazine may be used in determining the presence of the "carbonyl" group in a compound. (See p. 55.)

PREPARATION XXXVI.

CINNAMIC ACID, $C_9H_8O_2 = C_6H_5CH:CH.CO_2H$. (*Phenylacrylic Acid.*)

LITERATURE.—Bertagnini (1856), Ann. Ch. Pharm. 100, 126; Perkin (1868), Chem. Soc. J. 21, 53 and 185 and (1886) 47, p. 317; Fittig (1881), Ber. 14, 1826, and (1885) Ann. Ch. Pharm. 227, 79.

25 grms. benzaldehyde.
12·5 ,, sodium acetate (fused).
37·5 ,, acetic anhydride.

Twenty-five grms. benzaldehyde, 12·5 grms. sodium acetate, previously fused and powdered, and 37·5 grms. acetic anhydride are mixed together in a flask connected to a reflux condenser and kept at a gentle boil on the oil-bath for about eight hours. On cooling, water is added to the dark-coloured viscid liquid and a slight excess of sodium carbonate, and any unchanged benzaldehyde distilled off with steam. After filtering from undissolved resinous by-products, the addition of hydrochloric acid precipitates the free

solution of aniline hydrochloride well cooled in ice, and 15 grms. sodium nitrite dissolved in about 100 c.c. water added, the temperature of the mixture being kept at 0°. Diazobenzene chloride is formed, and the solution becomes cloudy from the separation of sodium chloride. To the mixture, which is still cooled in ice, 90 grms. commercial stannous chloride dissolved in about an equal weight of conc. hydrochloric acid are added. A thick white crystalline precipitate of phenylhydrazine hydrochloride almost immediately forms, and is separated from the mother-liquor by filtration. The free base is obtained by decomposing the hydrochloride with caustic soda. The former is therefore dissolved in a small quantity of hot water, an excess of caustic soda solution added and the mixture well shaken. The free base, which separates as a reddish-coloured oil, is extracted with ether, and the oily liquor, left on distilling off the ether, is dehydrated over anhydrous potassium carbonate and rectified.

$$\underset{\text{Aniline Hydrochloride}}{C_6H_5NH_2.HCl} + NaNO_2 + HCl = \underset{\text{Diazobenzenechloride.}}{C_6H_5N : N.Cl} + NaCl + 2H_2O$$

$$C_6H_5N : N.Cl + SnCl_2 + HCl = \underset{\text{Phenylhydrazine,}}{C_6H_5NH.NH_2} + SnCl_4$$

Properties.—Faint yellow-coloured oil, which solidifies in the cold to tabular crystals; m. p. 23°; b. p. 233—234°; sp. gr. 1·091 at 21°; scarcely soluble in cold water, more readily in hot water; almost inso-

luble in concentrated solutions of the alkalies ; easily soluble in alcohol, ether, and benzene. Phenylhydrazine may be used in determining the presence of the "carbonyl" group in a compound. (See p. 55.)

PREPARATION XXXVI.

CINNAMIC ACID, $C_9H_8O_2 = C_6H_5CH:CH.CO_2H$.
(Phenylacrylic Acid.)

LITERATURE.—Bertagnini (1856), Ann. Ch. Pharm. 100, 126; Perkin (1868), Chem. Soc. J. 21, 53 and 185 and (1886) 47, p. 317; Fittig (1881), Ber. 14, 1826, and (1885) Ann. Ch. Pharm. 227, 79.

25 grms. benzaldehyde.
12·5 „ sodium acetate (fused).
37·5 „ acetic anhydride.

Twenty-five grms. benzaldehyde, 12·5 grms. sodium acetate, previously fused and powdered, and 37·5 grms. acetic anhydride are mixed together in a flask connected to a reflux condenser and kept at a gentle boil on the oil-bath for about eight hours. On cooling, water is added to the dark-coloured viscid liquid and a slight excess of sodium carbonate, and any unchanged benzaldehyde distilled off with steam. After filtering from undissolved resinous by-products, the addition of hydrochloric acid precipitates the free

cinnamic acid in white crystalline flakes, which may be purified by recrystallisation from hot water.

$$\underset{\text{Benzaldehyde.}}{C_6H_5COH} + CH_3.CO_2Na = \underset{\text{Cinnamic Acid.}}{C_6H_5CH:CH.CO_2Na} + H_2O$$

Properties.—Colourless monoclinic prisms; m. p. 133°; b. p. 300—304°.

PREPARATION XXXVII.

HYDROCINNAMIC ACID, $C_9H_{10}O_2 = C_6H_5CH_2.CH_2CO_2H$.
(*Benzylacetic Acid, Phenylpropionic Acid.*)

LITERATURE.—Erlenmeyer, Alexejeff (1862), Ann, Ch. Pharm. 121, 375 and (1866) 137, 327.

10 grms. cinnamic acid.
100 „ water.
85 „ sodium amalgam (4 per cent.).[1]

[1] *Preparation of Sodium Amalgam.*—Twenty grms. well pressed sodium cut into small pieces are introduced into 500 grms. dry mercury (previously warmed) contained in a large Hessian crucible.* The formation of the amalgam is accompanied with evolution of heat and the sodium takes fire and burns. To prevent loss of mercury by spirting, the crucible is firmly closed with a lid. The solid amalgam is broken up into large pieces and preserved in a strong well-stoppered bottle.

Ten grms. cinnamic acid, to which 100 grms. water are added, are introduced into a stout flask or bottle of about ¼ litre capacity, and the liquid made slightly alkaline with caustic soda, which dissolves the greater part of the acid forming the sodium salt. A slight excess of the calculated quantity of 4 per cent. sodium amalgam (85 grms.) is added in small pieces from time to time, and the liquid thoroughly agitated. The solution, which remains clear, becomes slightly warm, and the amalgam soon liquefies; but no hydrogen is evolved until towards the end of the operation. When the whole of the amalgam has been added, and bubbles of gas cease to be given off, the alkaline solution containing the sodium salt of hydrocinnamic acid is poured off from the mercury, the latter is washed with water, and the washings added to the decanted portion. On acidifying the solution with hydrochloric acid, hydrocinnamic acid is precipitated as a colourless oil, which solidifies on cooling, and may be purified by crystallisation from water.

$$\underset{\text{Cinnamic Acid}}{C_6H_5CH:CH.CO_2H} + 2H = \underset{\text{Hydrocinnamic Acid.}}{C_6H_5CH_2.CH_2.CO_2H}$$

Properties.—Long colourless needles; m. p. 47°; b. p. 280°; soluble in water, alcohol, carbon bisulphide, and chloroform. Volatile in steam.

PREPARATION XXXVIII.

QUINOLINE, C_9H_7N.

LITERATURE.—Runge (1834), Pogg. Ann. 31, 65, 513 and 32, 308; Konigs (1880), Ber. 13, 911; Skraup (1880), Monatsh. 1, 316 (1881), 2, 141; (1881) Ber. 14, 1002.

24	grms.	nitrobenzene.
38	„	aniline.
120	„	glycerin.
100	„	conc. sulphuric acid.

Twenty-four grms. nitrobenzene, 38 grms. aniline, and 120 grms. glycerin, are mixed together in a round-bottomed flask of 1½–2 litre capacity, and 100 grms. conc. sulphuric acid gradually added. The mixture is carefully heated on the sand-bath with reflux condenser until the reaction begins (10–15 minutes), *i.e.* until white vapours rise from the liquid. The flask is now raised from the sand-bath, and, when the reaction is over, replaced, and the contents gently boiled with inverted condenser for 2–3 hours. The dark-coloured product is diluted with water and unchanged nitrobenzene driven over with steam. The residue is made strongly alkaline with caustic soda, and the oily layer (quinoline and aniline) which separates, distilled off with steam. In order to eliminate the aniline present, the distillate is acidified with

sulphuric acid and sodium nitrite added, until a sample of the liquid ceases to give the aniline reaction with bleaching powder solution. It is then boiled, whereby the aniline, converted into diazobenzene sulphate, is decomposed. The liquid is again made alkaline with caustic soda and submitted to a third distillation with steam. The distillate is extracted with ether, and, after driving off the ether, the residue is dehydrated over solid caustic potash, or potassium carbonate, and distilled.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Glycerin}}{C_3H_5(OH)_3} + O = \underset{\text{Quinoline.}}{C_9H_7N} + 4H_2O$$

The nitrobenzene acts as the oxidising agent.

Properties.—Colourless liquid; b. p. 237°; sp. gr. 1·108 at 0°.

PREPARATION XXXIX.

$$\text{MESITYLENE} = C_6H_3 \begin{matrix}(1)\ CH_3.\\(3)\ CH_3.\\(5)\ CH_3.\end{matrix}$$

(*Trimethylbenzene.*)

LITERATURE.—Kane (1840), Journ. Prakt. Ch. 15, 129; Fittig, Brückner (1868), Ann. Ch. Pharm. 147, 43.

250 grms. acetone.
560 „ conc. sulphuric acid mixed with $\frac{1}{2}$ volume of water.

One pound dry sand is brought into a 2-litre retort connected with a condenser. Upon this 250 grms. acetone are poured, and from a tap funnel inserted through the tubulus, a cooled mixture of 560 grms. conc. sulphuric acid and 150 grms. water are slowly run in, in an uninterrupted stream, the retort being immersed in cold water in case the reaction becomes too violent. The liquid, which forms a homogeneous mixture, is allowed to stand twenty-four hours, whereby it gradually assumes a brown colour. It is then distilled. At first, unchanged acetone, water, and a small quantity of mesitylene pass over. As soon as oily drops are observed in the neck of the retort, the receiver is changed. A yellow oil, consisting chiefly of mesitylene, distils with the aqueous vapour. The distillation is continued until inconsiderable quantities of the oil appear. The liquid in the retort meantime changes to deep brown, and finally to black, with evolution of sulphurous acid fumes, and froths up considerably. The distillate divides into two layers; the upper yellowish layer containing mesitylene is separated from the lower layer of water, washed with caustic soda and water, and dehydrated over calcium chloride. It is then fractionated (100-200°; 200-300°). On the first distillation a very small quantity of mesitylene distils at its boiling-point; but after three or four fractionations over thin slices of metallic sodium about two-thirds of the portion distilling at

100-200° is obtained as pure mesitylene boiling constantly at 163°.

$$\underset{\text{Acetone}}{3C_3H_6O} = \underset{\text{Mesitylene.}}{C_9H_{12}} + 3H_2O$$

Properties.—Colourless, strongly refracting liquid; b. p. 163°; sp gr. ·881 at 0°.

PREPARATION XL.

MESITYLENIC ACID, $C_9H_{10}O_2 = C_6H_3$ (1) CH_3. (3) CH_3. (5) $COOH$.

UVITIC ACID, $C_9H_8O_4 = C_6H_3$ (1) CH_3. (3) $COOH$. (5) $COOH$.

LITERATURE.—Fittig (1867), Ann. Ch. Pharm. 141, 144; Fittig, Brückner (1868), Ann. Ch. Pharm. 147, 292; Finck (1862), Ann. Ch. Pharm. 122, 184; Fittig, Furtenbach (1868), Ann. Ch. Pharm. 147, 295; Baeyer (1868), Zeitschr. 119.

20 grms. mesitylene.
33 ,, conc. nitric acid sp. gr. 1·4.
47 ,, water

Twenty grms. mesitylene contained in a round-bottomed flask of $\frac{1}{4}$ litre capacity, connected with reflux

condenser, are oxidised by boiling with a mixture of 33 grms. nitric acid sp. gr. 1·4 and 47 grms. water. After heating the whole on the sand-bath for 16 to 20 hours, the oxidation, which occurs with evolution of nitrous fumes, is complete, and the hydrocarbon is converted into a white, difficultly soluble, strongly acid substance. On cooling, the mass is filtered, washed with cold water and separated from unattacked mesitylene and also nitromesitylene by dissolving in sodium carbonate solution. On acidifying the alkaline solution with hydrochloric acid the acids are reprecipitated. Nitromesitylenic acid, which is also formed in the reaction, goes into solution on reduction with tin and strong hydrochloric acid. This operation must be conducted in a capacious flask, as the mass froths up, and should be heated for at least one hour, with constant shaking. On cooling, the undissolved portion is brought on to a filter, washed with cold water, dissolved in soda solution and reprecipitated from the hot filtered solution with hydrochloric acid. The white precipitate is a mixture of mesitylenic and uvitic acids. These are filtered and then separated from one another by distilling in steam. The distillation is continued until no further trace of mesitylenic acid appears in the condenser, and the distillate ceases to have an acid reaction. This occurs in the course of several hours. The larger portion of the

mesitylenic acid, free from uvitic acid, is contained suspended in the distillate, from which it may be separated by filtration. The filtrate is neutralised with soda solution, evaporated to a small bulk, precipitated with hydrochloric acid, and the usually somewhat yellow-coloured acid thus obtained united with the first portion. To purify it, the whole is redissolved in soda solution, and from the solution, filtered boiling hot, on the addition of hydrochloric acid in excess, colourless mesitylenic acid separates out, and by a single crystallisation from alcohol is pure. From the residual liquid in the distilling flask uvitic acid separates on cooling, containing traces only of mesitylenic acid, and is purified by recrystallisation from hot alcohol.

$$\underset{\text{Mesitylene}}{C_9H_{12}} + O_3 = \underset{\text{Mesitylenic Acid.}}{C_9H_{10}O_2} + H_2O$$

$$\underset{\text{Mesitylenic Acid}}{C_9H_{10}O_2} + O_3 = \underset{\text{Uvitic Acid.}}{C_9H_8O_4} + H_2O$$

Properties. — *Mesitylenic Acid* — Colourless monoclinic crystals; m. p. 166°; with difficulty soluble in hot water, readily soluble in cold alcohol. *Uvitic Acid*—Colourless fine needles; m. p. 287 to 288°; insoluble in cold and hot water, readily soluble in alcohol and ether.

PREPARATION XLI.

TRIPHENYLMETHANE, $C_{19}H_{16} = CH(C_6H_5)_3$

LITERATURE.—Kekulé, Franchimont (1872), Ber. 5, 907; Hemilian (1874), Ber. 7, 1204; Friedel, Crafts (1877), Compt. rend. 1450; E. and O. Fischer (1878), Ann. Ch. Pharm. 194, 252; Schwarz (1881), Ber. 14, 1516; Friedel, Crafts (1882), Bull. Soc. Chim. 37, 6

170 grms. benzene.
33 ,, chloroform.
50 ,, aluminium chloride.

Thirty-three grms. chloroform and 170 grms. benzene, both carefully dehydrated, are mixed together in a retort connected with a reflux condenser. Fifty grms. of aluminium chloride are added in portions of about 10 grms. at a time. On the addition of the chloride the reaction sets in spontaneously and the liquid begins to boil with copious evolution of hydrochloric acid. The aluminium chloride gradually dissolves, forming a dark brown oily liquid. When the aluminium chloride has been added, the mass is allowed to stand about twelve hours, and the reaction completed by heating for two hours on the sand-bath, when a further quantity of hydrochloric acid is evolved. The contents of the retort are cooled and poured into an equal volume of cold

water, which decomposes the aluminium triphenylmethane compound with evolution of heat and the free hydrocarbon dissolves in the excess of benzene with a reddish brown colour. The upper layer of benzene is separated from the aqueous portion, and the former dehydrated over calcium chloride. The excess of benzene is now distilled off on the water-bath, and the dark-coloured residual liquid fractionated up to 200° at the ordinary pressure, and finally *in vacuo*. This

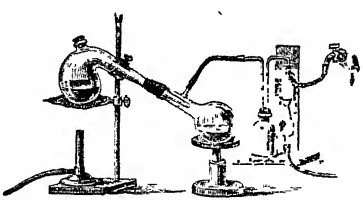


FIG 19.

operation is conducted in the apparatus shown in Fig. 19, and consists of a retort and receiver, the latter being in connection with a water-jet aspirator. At first an oily liquid distils. This is impure diphenylmethane. When most of the diphenyl compound has passed over the distillation suddenly slackens. The receiver is now changed, and the contents of the retort more strongly heated. An orange-coloured oil passes over, which crystallises in the receiver. The distillation is continued until the

distillate no longer solidifies on cooling. A black resinous mass remains in the retort. The crude triphenylmethane in the receiver is recrystallised from hot benzene, forming a crystalline molecular compound with the solvent of the formula $C_{19}H_{16}{\cdot}C_6H_6$, which separates out on cooling as a yellow crystalline mass. This is again crystallised from benzene. By heating the substance on the water-bath it loses benzene and the triphenylmethane which remains is finally crystallised from hot alcohol.

$$\underset{\text{Chloroform}}{CHCl_3} + 2\underset{\text{Benzene}}{C_6H_6} = \underset{\text{Triphenylmethane.}}{CH(C_6H_5)_3} + 3HCl$$

Properties.—Brilliant colourless plates; m. p. 92°; b. p. 360°; readily soluble in hot alcohol, in ether, and chloroform; with difficulty in cold alcohol. On dissolving in cold, fuming nitric acid, pouring into water and treating the precipitate with zinc dust and glacial acetic acid, leucaniline is formed. This is precipitated with ammonia, and on gently warming the dry precipitate with a few drops of hydrochloric acid on a piece of platinum foil the magenta coloration is obtained from the formation of rosaniline hydrochloride.

PREPARATION XLII.

ETHYL BENZOATE, $C_9H_{10}O_2 = C_6H_5CO.OC_2H_5$
(*Benzoic Ester.*)

LITERATURE.—Carius (1859), Ann. Ch. Pharm. 110, 210.

50 grms. alcohol (absolute).
25 ,, benzoic acid.

Fifty grms. absolute alcohol and 25 grms. benzoic acid are mixed together in a flask of about 250 c.c. capacity fitted with a double-bored cork. Through one hole a small upright condenser is inserted, through the other a delivery tube passes, which dips below the liquid in the flask. Through the delivery tube a rapid current of hydrochloric acid gas is conducted into the mixture of alcohol and benzoic acid.* The gas is most conveniently generated by dropping conc. sulphuric acid from a tap funnel into a flask half-filled with conc. hydrochloric acid. The temperature of the mixture, as the gas passed in, rises to the boiling point of the alcohol, and the benzoic acid quickly dissolves. When the first reaction is over and the contents of the flask begin to cool again, the vessel is placed on the water-bath and the current of gas continued until fumes of the acid escape from the upper

end of the condenser. The contents of the flask are now poured into water, when a colourless oil falls to the bottom. The oil is shaken with dilute sodium carbonate solution to dissolve unattacked benzoic acid, then with water, separated as carefully as possible from the latter and dehydrated over ignited potassium carbonate. It is decanted and distilled.

The product boils nearly constantly at 211°.

$$\underset{\text{Benzoic Acid}}{C_6H_5COOH} + C_2H_5OH = \underset{\text{Ethyl Benzoate.}}{C_6H_5CO_2C_2H_5} + H_2O.$$

Properties.—Colourless, oily liquid, with a pleasant fruity smell; b. p. 211·2°; sp. gr. 1·0502. Treated with conc. ammonia it yields benzamide and alcohol; boiled with caustic potash it splits up into its original constituents, benzoic acid (potassium salt) and alcohol (hydrolysis or saponification).

PART II.

PREPARATION XLIII.

Ethyl Bromide, C_2H_5 Br.

Literature—Serullas (1827), Ann. Ch. Phys. 34, 99; Personne (1861), Compt. rend. 52, 468.

10 grms. amorphous phosphorus.
60 ,, absolute alcohol.
60 ,, bromine.

10 grms. amorphous phosphorus are placed in a dry round-bottomed flask of about $\frac{1}{2}$ litre capacity, connected with condenser and receiver, together with 60 grms. commercial absolute alcohol; 60 grms. bromine are slowly run in from a tap funnel, the flask being cooled if necessary during the operation. After standing for a few hours the mixture is distilled on the water-bath, the temperature of which is slowly raised (Fig. 20). The reddish distillate, consisting of ethyl bromide and alcohol, is shaken with double the volume of water to which soda solution is added

until slightly alkaline. The ethyl bromide, which sinks to the bottom of the vessel, is drawn off by a tap funnel, and is then shaken repeatedly with water. It is separated as completely as possible from water and dehydrated over pieces of fused calcium chloride. The

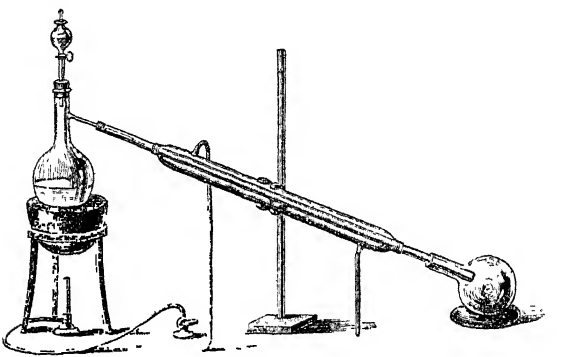


FIG. 20.

clear liquid after being decanted is distilled on the water-bath, a thermometer being inserted through the cork of the distilling flask. The ethyl bromide distils at 36-40° and may be further purified by a second distillation.

$$\underset{\text{Alcohol}}{5C_2H_5(OH)} + 5Br + P = \underset{\text{Ethyl Bromide.}}{5C_2H_5Br} + H_3PO_4 + H_2O$$

Properties.—Colourless liquid; b. p. 38·8°; sp. gr. 1·47 at 13·5°.

Determination of Specific Gravity.—A simple method for determining the specific gravity of liquids is as follows: A small glass bottle of about 20—30 c.c. capacity, which can be readily made by the help of the blow-pipe (Fig. 21), is fitted with a cork. The neck of the vessel just above the bulb is narrowed by drawing it out in the flame, and a horizontal mark *m*

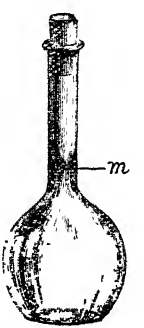


FIG. 21.

etched or scratched on it with a file. The bottle is thoroughly cleaned, dried in the air-bath, allowed to cool and weighed. It is then filled with the liquid, which is poured in through a funnel, the stem of which is drawn out so as to pass through the constricted neck. The bottle is placed in a mixture of snow or pounded ice and a little water and left $\frac{1}{4}$ to $\frac{1}{2}$ hour until the contents have a temperature of 0°. The meniscus is now

adjusted until it coincides with the mark on the neck of the bottle. If more liquid has to be added this may be done from a small pipette with capillary delivery tube; if some of the liquid has to be removed a piece of bibulous paper may be used to absorb it. The bottle is then corked, dried, allowed to remain ¼ hour in the balance case and weighed. It is then emptied, cleaned and dried and filled with distilled water previously boiled. The water is cooled to 0°, the meniscus adjusted and the bottle weighed, the same process being repeated as that just described. The following expression will give the specific gravity of the liquid at 0° compared with water at 4° and reduced to a vacuum.

$$S = \rho\frac{W_3 - W_1}{W_2 - W_1} + \sigma\frac{W_2 - W_3}{W_2 - W_1}$$

Where W_1 = apparent weight of the empty bottle.

W_2 = „ „ bottle and water at 0°

W_3 = apparent weight of the bottle and liquid at 0°

ρ = density of water at 0° = ·999873.

σ = density of air at t° (temperature of the balance room).

A very delicate and useful piece of apparatus, which is readily made with the blow-pipe, is Perkin's modification of Sprengel's specific gravity tube (*Chem.*

Soc. J. 45, 421). It is especially adapted for small quantities of liquid and for the more volatile ones. The apparatus (Fig. 22) consists of a U-tube to hold from 2 to 10 c.c., drawn out at each end into a fine capillary. The one capillary limb (*a*) is bent

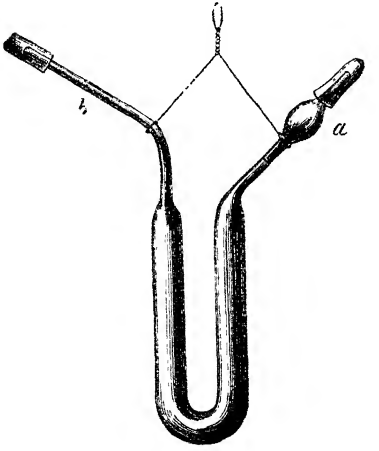


FIG. 22.

outwards and is furnished with a small bulb, the other (*b*) is bent at a right angle with the first. On the limb *a*, between the bulb and the top of the U-tube, a mark is scratched. The tube is dried and weighed, and the liquid drawn in through the limb *b* until it half fills the small bulb on the limb *a*. The apparatus

is cooled in pounded ice, and the meniscus adjusted to the mark on *a* by tilting the tube until the limb *b* has a horizontal position. To the end of this limb a piece of bibulous paper is applied until the liquid sinks to the desired position in the limb *a*. The U-tube is then brought to a vertical position, loose glass caps placed over the ends of the two limbs, the apparatus carefully dried, allowed to stand and weighed. The operation is then repeated with distilled water. An experiment with ethyl bromide gave the following results :

Weight of the tube empty	6·242	grms.
,, ,, + ethyl bromide at 0°	9·472	,,
,, ,, + water at 0°	8·417	,,

$$S = \cdot 99873 \times \frac{3 \cdot 230}{2 \cdot 175} = 1 \cdot 485$$

The correction for weight in air is so small that it may here be neglected.

PREPARATION XLIV.

ETHER, $C_4H_{10}O = C_2H_5OC_2H_5$.

(*Sulphuric Ether. Ethyl Oxide.*)

LITERATURE.—V. Cordus 1544; Boullay (1813), Journ. Pharm. 1, 97; Williamson (1850) Phil. Mag. (3), 37, 350.

300 grms. conc. sulphuric acid.
170 ,, absolute alcohol.

A mixture of 300 grms. conc. sulphuric acid and 170 grms. absolute alcohol are heated to 140° in a round-bottomed flask on wire gauze by means of a Bunsen lamp. The flask is closed with a cork pierced with 3 holes. Through one of these a thermometer is inserted and dips into the liquid; through the second

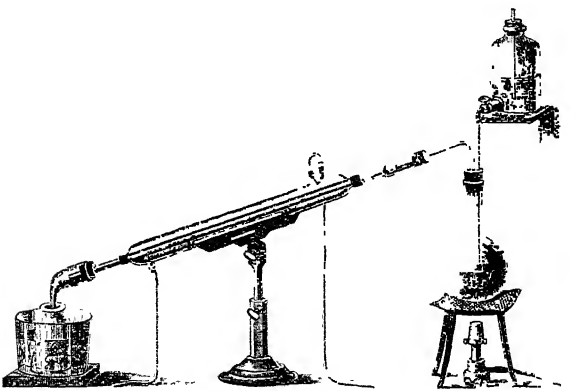


FIG. 23.

a tube is fitted which reaches just above the surface of the liquid and is attached at its upper end with a vessel containing alcohol (Fig. 23). A bent tube passing through the third hole connects the flask with a long condenser and receiver, both of which must be kept well cooled during the operation.

When the temperature of the mixture reaches 140°, 90 per cent. alcohol is run in from the reservoir of alcohol in proportion to the quantity of liquid which distils. The temperature must be maintained constant at 140-145°, which is easily effected by regulating the supply of alcohol. When about treble the quantity of alcohol contained in the original mixture has been converted into ether the distillation is stopped. The liquid in the receiver consists of two layers, and contains in addition to ether, alcohol, water and sulphurous acid. The ethereal layer is drawn off, washed with dilute soda solution, then repeatedly with water, and is dehydrated over pieces of fused calcium chloride. It is rectified on the water-bath. The ether thus purified still contains traces of alcohol and water, which it obstinately retains, and from which it can only be freed by a further treatment with metallic sodium (see p. 5). The ether may be finally distilled on the water-bath over fresh metallic sodium. The receiver in which the ether collects should be cooled with ice, and a calcium chloride tube attached to it to prevent absorption of moisture during the distillation.

$$C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl Sulphate.}}{C_2H_5.SO_4H} + H_2O$$

$$C_2H_5.SO_4H + C_2H_5OH = \underset{\text{Ether.}}{C_2H_5OC_2H_5} + H_2SO_4$$

On heating alcohol and sulphuric acid, ethyl sulphate is first formed with elimination of water. In the second phase of the

reaction, which occurs at 140°, a second molecule of alcohol is decomposed with the formation of ether, sulphuric acid being regenerated, and the latter can again convert a fresh quantity of alcohol into ether.

Properties.—Colourless, mobile liquid; b. p. 35°; sp. gr. ·713 at 20°; burns with a luminous flame. Not miscible with water; 9 parts water dissolve 1 part ether.

PREPARATION XLV.

CHLOROFORM, $CHCl_3$

LITERATURE.—Liebig (1831), Pogg. Ann. 23, 444; Soubeiran (1832), Ann. Ch. Phys. (2), 48, 131; Dumas (1834), Ann. Ch. Phys. 56, 115.

200 grms. bleaching powder.
800 ,, water.
33 ,, alcohol (absolute).

Two hundred grms. bleaching powder, 800 grms. water, and 33 grms. absolute alcohol are placed in a round-bottomed flask connected with a condenser and well mixed into a paste. The mass is carefully heated on the water-bath. As soon as the reaction begins, chloroform and water commence to distil over into the receiver, where the former settles to the bottom as a heavy oil. When no more chloroform distils, the distillate is shaken with dilute caustic soda, separated

and dehydrated over calcium chloride. It is finally rectified on the water-bath.

$$\underset{\text{Calcium Hypochlorite}}{4Ca(OCl)_2} + \underset{\text{Alcohol}}{2C_2H_5(OH)} = \underset{\text{Chloral.}}{2CCl_3CHO} + CaCl_2 + 3Ca(OH)_2 + 2H_2O$$

$$\underset{\text{Chloral}}{2CCl_3CHO} + Ca(OH)_2 = \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium Formate.}}{Ca(HCO_2)_2}$$

The formation of chloroform is here due to a secondary reaction. By the action of bleaching powder on alcohol, choral is first formed, which decomposes in presence of the calcium hydrate of the bleaching powder into chloroform and calcium formate.

Properties.—Colourless liquid possessing an ethereal odour and sweet taste; b. p. 62°; sp. gr. 1·525 at 0°; does not burn.

PREPARATION XLVI.

ETHYL ORTHOFORMATE, $C_7H_{16}O_3 = CH(OC_2H_5)_3$

LITERATURE—Williamson, Kay (1854), Proc. Roy. Soc. 7, 135; Basset (1864), Chem. Soc. J. (2) 198; Ladenburg, Wichelhaus (1869), Ann. Ch. Pharm. 152, 164; Deutsch (1879), Ber. 12, 116.

100 grms. chloroform.
117 „ absolute alcohol.
58·5 „ sodium.
350 c.c. anhydrous ether.

58·5 grms. metallic sodium well pressed between filter paper and cut into thin slices are added in

small portions at a time to a mixture of 100 grms. chloroform, 117 grms. absolute alcohol and 350 c.c. dry ether contained in a $1\frac{1}{2}$ litre flask which is attached to a reflux condenser. At the commencement the reaction proceeds rather violently and the flask must be *well cooled* with ice. The clear liquid becomes gradually thick from the separation of sodium chloride and changes to a brown colour. The reaction is completed by warming the mass on the water-bath with inverted condenser until the whole of the sodium is converted into sodium chloride. The contents of the retort are poured into water whereby the ethyl orthoformate dissolved in the ether separates out on the surface of the water in the form of a brown liquid. The ethereal solution is drawn off, well washed with water, separated from the aqueous layer and dehydrated over calcium chloride. It is then distilled on the water-bath, and when no further liquid passes over the distillation is continued over the bare flame. The distillate passing over above 110° is redistilled and the orthoformic ether is then pure.

$$\underset{\text{Chloroform}}{CHCl_3} + 3\underset{\text{Alcohol}}{C_2H_5OH} + 3Na = \underset{\text{Ethyl Orthoformate}}{CH(OC_2H_5)_3} + 3NaCl + 3H$$

Properties—Colourless liquid; b. p. 145-147°; sp. gr. ·8964.

PREPARATION XLVII.

POTASSIUM ETHYL SULPHATE, $C_2H_5O_4SK = C_2H_5O.SO_2OK$.

LITERATURE.—Berthelot (1855), Ann. Ch. Phys. (3) 43, 385; Claesson (1879), Journ. Prakt. Ch. (2) 19, 246.

100 grms. absolute alcohol.
75 „ conc. sulphuric acid.

To 100 grms. commercial absolute alcohol contained in a porcelain basin about ½ litre capacity, 75 grms. conc. sulphuric acid are slowly added and the two layers quickly mixed, whereby the temperature rises to 80—90°. The mixture is heated for a short time on the water-bath. The product then contains in addition to the acid ether, free sulphuric acid and unchanged alcohol. On cooling, the liquid is diluted by first adding ice to prevent any great increase of temperature, and then water. It is neutralised with chalk ground into a paste with water. The filtered solution of calcium ethyl sulphate made slightly alkaline with lime water, may be concentrated on the water-bath without fear of decomposition. By adding a concentrated solution of potassium carbonate until the calcium is just precipitated, the soluble potassium salt of ethyl sulphate is formed, which is separated by filtration from the precipitated calcium carbonate.

The clear solution, with the addition of a small quantity of potassium carbonate, can be evaporated without decomposition on the water-bath until crystallisation begins. By slowly concentrating the liquid a well crystallised product may be obtained.

$$C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl Sulphate.}}{C_2H_5SO_4H} + H_2O.$$

$$2C_2H_5SO_4H + CaCO_3 = \underset{\text{Calcium Ethyl Sulphate.}}{(C_2H_5SO_4)_2Ca} + H_2O + aCO_2$$

$$(C_2H_5SO_4)_2Ca + K_2CO_3 = \underset{\text{Potassium Ethyl Sulphate.}}{2C_2H_5SO_4K} + CaCO_3$$

Properties.—Colourless, foliated crystals; easily soluble in water and dilute alcohol; insoluble in absolute alcohol and ether.

PREPARATION XLVIII.

PROPIONITRIL, $C_3H_5N = C_2H_5CN$.
(*Ethyl Cyanide.*)

LITERATURE.—Pelouze (1834), Ann. Ch. Pharm. 10, 249: Linnemann (1868), Ann. Ch. Pharm. 148, 252; Rossi (1871), Ann. Ch. Pharm. 159, 79.

50 grms. potassium ethyl sulphate
50 „ potassium cyanide [pure].

Fifty grms. finely powdered potassium ethyl sulphate dried at 100°, and 50 grms. dry powdered pure potassium cyanide are thoroughly mixed and

introduced into a stout glass tube closed at one end, which is two-thirds filled with the mixture. A small channel is formed along the upper surface to allow the gaseous products to escape by tapping the tube horizontally. The tube is placed in a combustion furnace, the open end of which should project about 3 cm. from the furnace (Fig. 17) and is connected with a condenser and receiver. The mixture is carefully subjected to dry distillation, beginning at the front end and proceeding gradually towards the closed end of the tube. The yellowish brown oily distillate,[1] which possesses an unpleasant smell, is re-distilled, and the portion passing over below 110° and consisting of propionitril, isopropionitril, alcohol, and water, collected. Isopropionitril is dissolved out by shaking the distillate with a small quantity of conc. hydrochloric acid. The oil floating on the surface of the acid is separated, washed with a small quantity of water, dehydrated with calcium chloride and anhydrous potassium carbonate, and then distilled. The propionitril dissolved in the washings may be separated by adding calcium chloride.

$$\underset{\text{Potassium Ethyl Sulphate.}}{C_2H_5SO_4K} + KCN = \underset{\text{Propionitril.}}{C_2H_5CN} + K_2SO_4$$

Properties.—Colourless liquid having a peculiar ethereal smell; b. p. 98°; sp. gr. 0·789 at 12°; somewhat soluble in water.

[1] This may be at once converted into propionic acid, see Prep. XLIX., without further purification.

PREPARATION XLIX.

PROPIONIC ACID, $C_3H_6O_2 = CH_3.CH_2.CO.OH$.

LITERATURE.—Gottlieb (1844), Ann. Ch. Pharm. 52, 127; Frankland, Kolbe (1848), Chem. Soc. J. 1, 60; Ann. Ch. Pharm. 65, 269; Williamson (1853), Phil. Mag. (4) 6, 204; Rossi (1871), Ann. Ch. Pharm. 159, 79; Beckurts, Otto (1877), Ber. 10, 262.

50 grms. propionitril

150 ,, mixture of { 2 vol. water and 3 vol. conc. sulphuric acid.

To 50 grms. ethylcyanide contained in a round-bottomed flask of about 1½ litre capacity, and connected with a reflux condenser, 150 grms. of a mixture of 2 vol. water and 3 vol. conc. sulphuric acid are slowly added and allowed to stand for some time. The mixture is then heated to 100° without disconnecting the condenser. The originally clear liquid becomes cloudy owing to the separation of propionic acid, which is insoluble in the solution of ammonium sulphate formed during the reaction. When no more oil separates out on the surface of the liquid (with 50 grms. of the cyanide about 12 hours heating is necessary) the reaction is complete. After allowing the liquid to cool down to 50°, the almost colourless acid is separated and purified by distillation.

$$\underset{\text{Ethyl Cyanide}}{2C_2H_5CN} + H_2SO_4 + 4H_2O = \underset{\text{Propionic Acid.}}{2C_2H_5COOH} + (NH_4)_2SO_4$$

Properties.—Colourless liquid possessing a smell similar to that of acetic acid; b. p. 140·7°; sp. gr. 1·016 at 0°; soluble in water; the acid may be separated from its aqueous solution as an oily layer by the addition of calcium chloride.

PREPARATION L.

ETHYLENE DIBROMIDE, $C_2H_4Br_2 = CH_2Br.CH_2Br$

LITERATURE.—Balard (1826), Ann. Ch. Phys. (2) 32, 375; Erlenmeyer, Bunte (1873) Ann. Ch. Pharm. 168, 64; Erlenmeyer) 1878), Ann. Ch. Pharm. 192, 244.

25 grms. alcohol
150 „ conc. sulphuric acid.

A mixture of 25 grms. strong alcohol and 150 grms. conc. sulphuric acid are heated in a 2-litre round-bottomed flask on a sand-bath until ethylene vapour is evolved in a steady stream. A mixture of 1 part alcohol and 2 parts conc. sulphuric acid are run into the flask through a tap funnel at such a speed that the stream of gas continues without interruption, and at the same time without causing the contents of the vessel to froth up too violently. The gas is purified from alcohol, ether, sulphurous acid, and carbonic acid, by conducting it through a series of Woulff's bottles fitted with safety tubes and connected with the generating flask (Fig. 24). The first of these

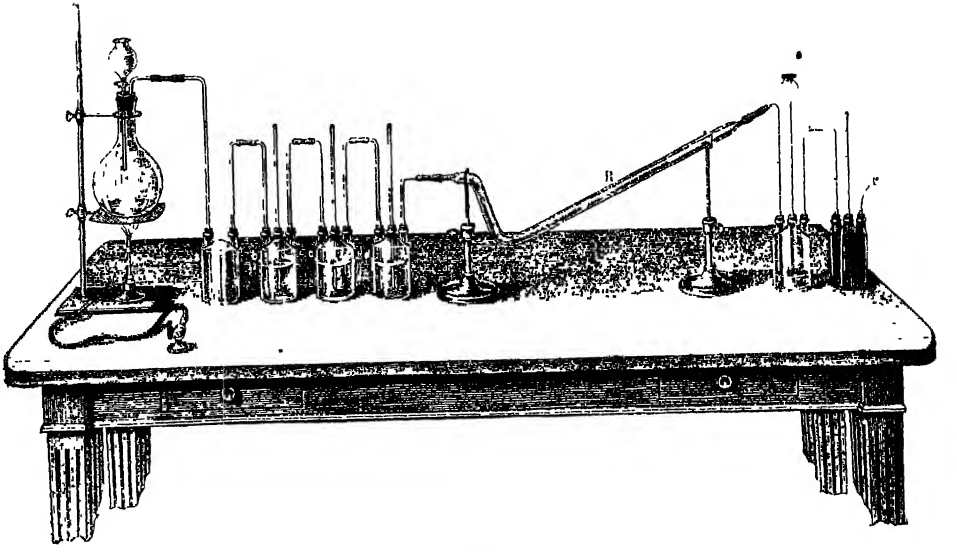


FIG. 24.

bottles (*a*) is empty, the second (*b*) contains conc. sulphuric acid, the third (*c*) and fourth (*d*) dilute caustic soda solution. Thus purified, the ethylene passes into a long bent tube (R)[1] and a Woulff's bottle (*e*), which contain bromine covered with a layer of water. The tube (R) contains 150 grms. bromine and 1 c.c. water, and the bottle (*e*) 50 grms. bromine and 1 c.c. water. The last bottle is filled to a height of 5 cm. with broken glass, and then with lumps of dry soda-lime. As soon as the bromine assumes a pale yellow tint by absorption of ethylene and conversion into ethylene bromide, the evolution of gas is interrupted or the liquid removed and a fresh quantity of bromine introduced. The crude ethylene bromide is shaken with dilute caustic soda solution, washed with water, separated from the aqueous layer and dehydrated over calcium chloride. After decanting from the calcium chloride it is rectified.

$$\underset{\text{Alcohol}}{C_2H_5(OH)} - H_2O = \underset{\text{Ethylene.}}{C_2H_4}$$

$$C_2H_4 + 2Br = \underset{\text{Ethylene Bromide.}}{C_2H_4Br_2}$$

Properties.—Colourless liquid which solidifies at 0° to a crystalline mass and melts at 9°; b. p. 129·5°; sp. gr. 2·17 at 20°.

[1] This may be replaced by a Woulff bottle, and cooled if necessary in cold water.

PREPARATION LI.

ETHYLENE ALCOHOL, $C_2H_6O_2 = CH_2(OH).CH_2(OH)$.
(*Ethylene Glycol.*)

LITERATURE.—Wurtz (1856), Compt. rend. 43, 199; Atkinson (1858), Phil. Mag. (4), 16, 433; Simpson (1859), Proc. Roy. Soc. 9, 725; Erlenmeyer (1874), Ann. Ch. Pharm. 173, 117 and (1875) 177, 145 and (1878) 192, 244; Zeller, Hüfner (1874), Journ. Prakt. Ch. (2) 10, 271 and (1875) (2) 11, 229.

94 grms. ethylene bromide.
69 ,, potassium carbonate.
½ litre water.

Ninety-four grms. ethylene bromide, 69 grms. potassium carbonate, and ½ litre water are heated to boiling in a litre round-bottomed flask on the sand-bath with reflux condenser. The boiling is continued until the whole of the ethylene bromide has disappeared, which occurs in about 10 hours. Carbonic acid and vinyl bromide (C_2H_3Br) are evolved. The latter may be collected as monobromethylene bromide by attaching to the upper part of the condenser a Liebig bulb apparatus containing bromine. When the reaction is finished, the contents of the vessel, while still warm, are poured into a porcelain basin and carefully concentrated on the water-bath until potassium bromide begins to separate out in considerable quantity. The cooled

mass is mixed into a paste with strong alcohol, and the alcoholic solution of glycol separated from potassium bromide by draining the mass at the filter-pump and washing well with strong alcohol. The alcohol is distilled off from the filtrate on a brine-bath and the residue on the oil-bath. The portion boiling at 185—205° is separately collected and re-distilled.

$$\underset{\text{Ethylene Bromide}}{C_2H_4Br_2} + K_2CO_3 + H_2O = \underset{\text{Ethylene Glycol.}}{C_2H_4(OH)_2} + 2KBr + CO_2$$

$$C_2H_4Br_2 + K_2CO_3 = \underset{\text{Vinyl Bromide.}}{C_2H_3Br} + KBr + KHCO_3$$

$$C_2H_3Br + 2Br = \underset{\text{Bromethylene Bromide.}}{C_2H_3Br_3}$$

Properties.—Syrupy liquid; b. p. 197·5°; sp. gr. 1·125 at 0°; soluble in water and alcohol.

PREPARATION LII.

ETHYLENE CHLORHYDRIN, $C_2H_3ClO = CH_2Cl.CH_2(OH)$.

(*Ethylene Chlorhydrate.*)

LITERATURE.—Wurtz (1859), Ann. Ch. Phys. (3) 55, 400; Carius (1862), Ann. Ch. Pharm. 122, 73 and (1862) 124, 257; Fittig, Chanlaroff (1884), Ann. Ch. Pharm. 226, 326.

50 grms. glycol.

125 „ chloride of sulphur.[1]

[1] *Preparation of Chloride of Sulphur.*—One hundred grms. sulphur are melted over a small flame in a dry retort of about

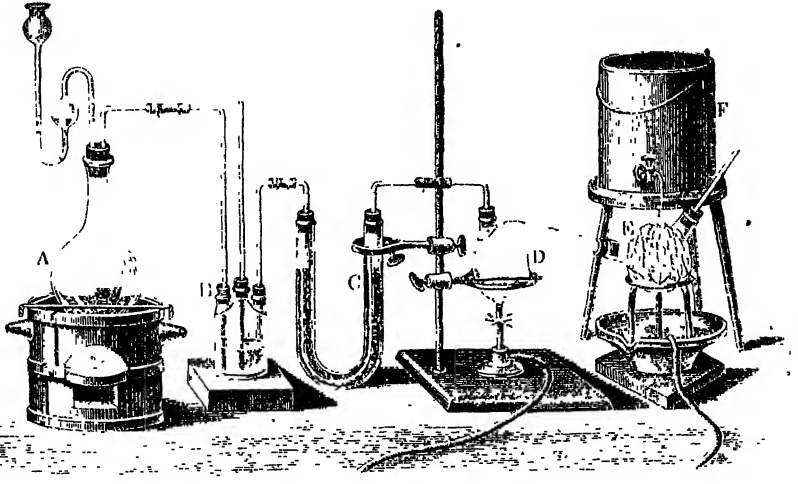


FIG. 25

One hundred and twenty-five grms. chloride of sulphur are added to 50 grms. glycol boiling at 196–198° contained in a dry round-bottomed flask of about ½ litre capacity, and the mixture is heated on the water-bath with a reflux condenser until the evolution of hydrochloric acid ceases, an operation which requires three or four days.* After cooling, the contents of the flask are extracted several times with ether, which readily dissolves out the chlorhydrin and the ethereal solution is decanted from precipitated sulphur. It is shaken for a time with moist potassium carbonate. The ether is then distilled off on the water-bath, and the distillation continued over a lamp. The portion, which passes over at 128–131°, is nearly pure ethylene chlorhydrin.

$$2C_2H_4(OH)_2 + 2S_2Cl_2 = 2C_2H_4\begin{matrix}Cl\\OH\end{matrix} + 2HCl + 3S + SO_2$$

Glycol Chloride of Sulphur Ethylene Chlorhydrin.

Properties.—Colourless liquid; b. p. 130–131°; sp. gr. 1·24 at 8°.

½ litre capacity connected with a receiver furnished with an exit tube. Into the melted sulphur, chlorine, dried by passing through conc. sulphuric acid and fused calcium chloride, is conducted, and chloride of sulphur distils over (Fig. 25). When the greater portion of the sulphur has been converted into chloride the evolution of gas is stopped. In the receiver a brownish yellow liquid collects, and is redistilled. The portion passing over at 138°—139° is pure chloride of sulphur.

Properties.—A reddish-yellow liquid; b. p. 139°; sp. gr. 1·68. Fumes in the air, and decomposes with water into sulphurous acid, hydrochloric acid, and water. This liquid is best preserved in sealed vessels.

PREPARATION LIII.

SUCCINIC ACID, $C_4H_6O_4 = COOH.CH_2.CH_2.COOH$. (*Ethylenedicarboxylic Acid.*)

LITERATURE.—Simpson (1860), Proc. Roy. Soc. 10, 574; Geuther (1861), Ann. Ch. Pharm. 120, 268.

100 grms. ethylene bromide,
75 ,, potassium cyanide.

One hundred grms. ethylene bromide and 75 grms. potassium cyanide in alcoholic solution are heated together on the water-bath in a round-bottomed flask of about ¾-litre capacity connected with reflux condenser. This process is continued until the potassium cyanide is converted into bromide, which separates out from the solution. To the alcoholic solution, filtered from potassium bromide, the calculated quantity of caustic potash (about 70 grms.) is added, and the mixture is heated on the water-bath with an upright condenser until the strong evolution of ammonia gas begins to slacken. The cooled contents of the flask are acidified with dilute hydrochloric acid and carefully evaporated to dryness. The dry powdered residue is extracted several times with absolute alcohol. On distilling off the alcohol the succinic acid remains behind in small crystals. The product, which is slightly coloured, is re-crystal-

lised from hot water (with the addition, if necessary, of animal charcoal) and, on cooling, forms colourless crystals.

$$\underset{\text{Ethylene Bromide.}}{C_2H_4Br_2} + 2KCN = \underset{\text{Ethylene Cyanide.}}{C_2H_4(CN)_2} + 2KBr$$

$$C_2H_4(CN)_2 + 2KOH + 2H_2O = \underset{\text{Potassium Succinate.}}{C_2H_4(COOK)_2} + 2NH_3$$

$$C_2H_4(COOK)_2 + 2HCl = \underset{\text{Succinic Acid}}{C_2H_4(COOH)_2} + 2KCl$$

Properties.—Colourless prisms which sublime above 100° without decomposition; m. p. 180°; at 235° the acid decomposes forming the anhydride; soluble in water, alcohol, and ether; insoluble in chloroform.

PREPARATION LIV.

DIBROMSUCCINIC ACID, $C_4H_4Br_2O_4$ = COOH.CHBr.CHBr.COOH.

LITERATURE.—Kekulé (1861), Ann. Ch. Pharm. 117, 120 and (1861) Spt. 1, 351; Burgoin (1873), Bull. Soc. Chem. 19, 148.

12 grms. succinic acid.
33 ,, bromine.
12 ,, water.

Twelve grms. succinic acid, 32 grms. bromine, and 12 grms. water are heated in a sealed tube with capillary end, on the air-bath, for six hours at 170°

(Fig. 26). On cooling, the tube is opened by wrapping it tightly in a cloth and softening the capillary end

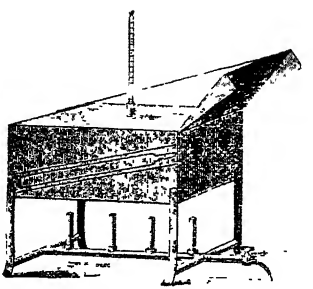


FIG. 26.

in the flame, when the pressure of gas within forces an outlet (Fig. 27). Hydrobromic acid escapes.

FIG. 27.

The red colour of the bromine has completely disappeared, and the tube is filled with a solid greyish white mass. By recrystallising the product from

boiling water, with the addition of a little animal charcoal, dibromsuccinic acid is obtained pure, in perfectly colourless well-defined crystals.

$$\underset{\text{Succinic Acid}}{C_4H_6O_4} + 4Br = \underset{\text{Dibromsuccinic Acid.}}{C_4H_4Br_2O_4} + 2HBr$$

Properties.—Colourless glistening crystals; difficultly soluble in cold, more readily in hot water, soluble in alcohol and ether; decompose at 200°, with formation of hydrobromic acid and brommaleic acid.

PREPARATION LV.

ACETALDEHYDE, $C_2H_4O = CH_3CHO$.
(*Aldehyde.*)

LITERATURE.—Liebig (1835), Ann. Ch. Pharm. 14, 133; Staedeler (1859), Journ. Prakt. Ch. (1), 76, 54.

100 grms. potassium dichromate.
420 ,, water.
100 ,, alcohol (absolute).
140 ,, conc. sulphuric acid.

One hundred grms. potassium dichromate broken into pieces, about the size of a coffee bean, and 420 grms. water are placed in a round-bottomed flask of about 2 litre capacity, connected with a con-

denser and receiver, the latter being well cooled with ice. To the cooled mixture a solution of 100 grms. alcohol (absolute) and 140 grms. conc. sulphuric acid, also well cooled, is slowly added from a tap-funnel, and the flask well shaken. A considerable

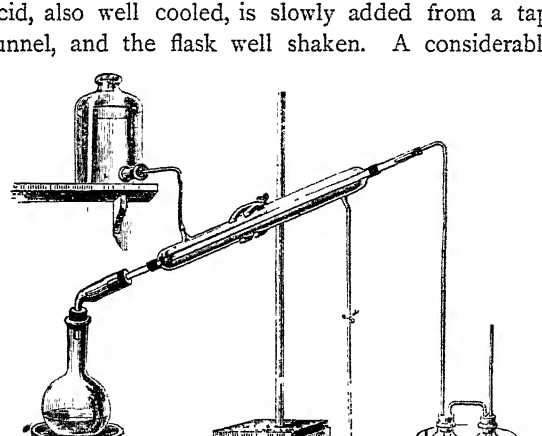


Fig. 28.

evolution of heat occurs, the liquid becomes green, and water, alcohol and aldehyde distil over into the receiver. The mixture is then heated on a sand-bath until all the aldehyde has distilled (about 150 c.c.). The distillate is now rectified on the water-

bath at a gentle heat (about 50°), and the vapours are led into an inverted condenser, in which the water is maintained at a temperature of 25—30°. Alcohol and aqueous vapour condense in the tube, the aldehyde, on the other hand, passes by a bent tube (preferably with a bulb about the middle to prevent ether being drawn over into the flask) into two vessels half filled with anhydrous ether (Fig. 28). The aldehyde

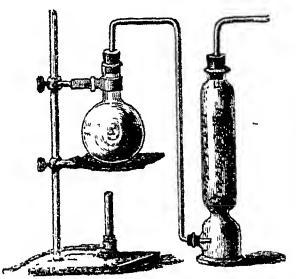


FIG. 29.

readily dissolves in the ether. If the ethereal solution be now saturated with ammonia gas, previously dried through quicklime (Fig. 29), the whole of the aldehyde separates out in the form of aldehyde ammonia as a white crystalline body. It is separated from the mother-liquor by draining well at the filter-pump, repeatedly washing with ether, and finally drying the crystals on bibulous paper over calcium

chloride. From the aldehyde-ammonia thus obtained pure aldehyde may be prepared. The crystals are dissolved in an equal weight of water, and distilled on the water-bath with a mixture of $1\frac{1}{2}$ parts conc. sulphuric acid and 2 parts water, the receiver, which is attached to the condenser, being cooled with ice.

The temperature of the water-bath is gradually raised until the water begins to boil, and the distillation is then interrupted. The distillate is dehydrated over an equal bulk of calcium chloride in coarse lumps, and again distilled over calcium chloride, the temperature of the water-bath being raised to 30°. The anhydrous acetaldehyde is kept in sealed tubes.

$$\underset{\text{Alcohol}}{3C_2H_5(OH)} + K_2Cr_2O_7 + 4H_2SO_4 = \underset{\text{Acetaldehyde.}}{3C_2H_4O} + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

$$C_2H_4O + NH_3 = CH_3CH\overset{OH}{\underset{NH_2}{}}$$

Aldehyde Ammonia.

$$2CH_3CH\overset{OH}{\underset{NH_2}{}} + H_2SO_4 = \underset{\text{Aldehyde.}}{2CH_3CHO} + (NH_4)_2SO_4$$

Properties.—Colourless liquid; b. p. 21°; sp. gr. ·807 at 0°; soluble in water, alcohol, and ether; it has a strong reducing action, and precipitates metallic silver from ammoniacal silver solution in the form of a mirror. If a solution of magenta in water is decolorised by passing in sulphur dioxide, a few drops of aldehyde restore the colour. (Schiff's reaction.)

PREPARATION LVI.

ACETYL CHLORIDE, $C_2H_3O.Cl = CH_3CO.Cl$.

LITERATURE.—Gerhardt (1853) Ann. Ch. Phys. (3) 37, 285, Béchamp (1855), Compt. rend. 40, 944; and (1856) 42, 224; Fittig (1886), Grundriss der Org. Chem. p. 116.

100 grms. glacial acetic acid.
80 „ phosphorus trichloride.[1]

To one hundred grms. glacial acetic acid contained in a dry round-bottomed flask of ½ to ¾ litre

[1] *Preparation of Phosphorus Trichloride.**—A retort of about ¾ litre capacity, the bottom of which is covered with a thin layer of dry sand, is connected with a receiver provided with an exit tubulus. One hundred grms. dry phosphorus in the form of small cubical pieces (it is cut in a mortar under water) are then introduced, over the surface of which chlorine gas is conducted. The phosphorus takes fire in the chlorine and burns with a lambent flame, forming phosphorus trichloride which collects in the well-cooled receiver. In the course of the operation, and while the chlorine is passing through at a good speed, the sides of the vessel must remain transparent. The chlorine inlet tube is movable in the cork, so that it may be raised or lowered readily. If the tube is too close to the surface of the phosphorus the latter becomes so strongly heated that dense fumes are evolved which cover the upper part of the retort with a layer of red phosphorus; and if, on the other hand, the tube is too far removed, phosphorus pentachloride is formed, which forms a yellow crystalline crust on the sides of the vessel. The position of the tube must be regulated so that neither the one nor the other reaction occurs. If a red deposit forms the tube must be slightly raised, if the pentachloride is produced it is lowered. The distillate is then rectified on the water-bath.

capacity, 80 grms. phosphorus trichloride are slowly added, the flask being well cooled.* The flask, to which a reflux condenser is now attached, is heated to about 40° on the water-bath.* When the evolution of hydrochloric acid gas has nearly ceased, the contents of the flask are distilled on the water-bath, the receiver being cooled in ice and provided with a calcium chloride tube to prevent absorption of moisture. Acetyl chloride collects in the receiver as a colourless liquid, which, after redistillation, is nearly pure, and should be kept in sealed vessels.

$$\underset{\text{Acetic Acid}}{3CH_3CO_2H} + PCl_3 = \underset{\text{Acetyl Chloride.}}{3CH_3COCl} + P(OH)_3$$

Properties.—Colourless liquid; b. p. 55°; sp. gr. 1·1305 at 0°; decomposes with water, forming hydrochloric acid and acetic acid, and therefore fumes in moist air.

The same arrangement of apparatus is employed as shown in Fig. 25. For the preparation of chlorine a mixture of broken pieces of pyrolusite and comm. conc. hydrochloric acid (heated preferably in an earthenware vessel in the water-bath) or a mixture of equal parts of powdered salt (600 grms.) and powdered manganese dioxide (600 grms.) may be employed. The latter is introduced into a round-bottomed flask of about 6 litres capacity, and a cooled mixture of 1440 grms. conc. sulphuric acid and 720 grms. water added. When the evolution of chlorine slackens the flask is heated on the sand-bath.

Properties.—Colourless liquid; b. p. 74°; sp. gr. 1·616 at 0°; fumes in moist air, decomposes into phosphorus acid and hydrochloric acid.

PREPARATION LVII.

ACETIC ANHYDRIDE, $C_4H_6O_3 = \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O$.

(*Acetyl Oxide.*)

LITERATURE.—Gerhardt (1853), Ann. Ch. Phys. (3) 37, 311.; Kanonikoff, Saytzeff (1877), Ann. Ch. Pharm. 185, 192.

80 grms. sodium acetate (fused).

50 „ acetyl chloride.

Eighty grms. anhydrous and powdered sodium acetate are introduced into a retort of about ¼ litre capacity, connected with a condenser and receiver, 50 grms. acetyl chloride are then slowly added, drop by drop, from a tap-funnel, the retort being well cooled.* When the reaction, which proceeds at the ordinary temperature, has ceased, the vessel is first heated on the water-bath and the anhydride is then distilled off on the sand-bath. The distillate is rectified, and the portion passing over at 135—140° collected. By a further distillation the pure anhydride is obtained, which must be kept in well-stoppered bottles.

$$CH_3CO_2Na + CH_3COCl = (CH_3CO)_2O + NaCl$$

Sodium Acetate Acetyl Chloride Acetic Anhydride.

Properties.—Colourless liquid, having an irritating smell; b. p. 138°; sp. gr. 1·097 at 0°; decomposes rapidly in presence of water into acetic acid.

PREPARATION LVIII.

ACETAMIDE, $C_2H_5NO = CH_3CO.NH_2$

LITERATURE.—Dumas (1847), Compt. rend. 25, 657; Kündig (1858), Ann. Ch. Pharm. 105, 277; Smit (1875), Bull. Soc. Chim. 24, 540; Hofmann, Buckton (1856), Ann. Ch. Pharm. 100, 131; Hofmann (1882), Ber. 15, 981.

100 grms. ammonium acetate.

One hundred grms. ammonium acetate (prepared by adding to 70 grms. glacial acetic acid warmed in a basin on the water-bath about 80 grms. powdered ammonium carbonate until the acid is neutralised) are heated for from 5 to 6 hours in sealed tubes to 230°. Tubes made from the usual thick-walled tubing may be filled half full of the salt without risk of bursting. The tubes then contain an oily-looking liquid, consisting of an aqueous solution of ammonium acetate, together with a large quantity of acetamide. The contents are distilled, and the portion boiling above 180° collected apart. This distillate, on standing, almost completely solidifies to a colourless crystalline mass. It is freed from mother-liquor by draining at the filter-pump, and purified by a second distillation.

The acetamide has then a nearly constant boiling point.

$$CH_3.COONH_4 = CH_3CONH_2 + H_2O$$

Properties. — Colourless rhombohedral crystals having a peculiar smell; m. p. 82°; b. p. 222°; easily soluble in water and alcohol.

PREPARATION LIX.

METHYLAMINE HYDROCHLORIDE, $CH_6NCl = CH_3NH_2HCl$.

LITERATURE.—Wurtz (1848), Compt. rend. 28, 223; Hofmann (1849), Ann. Ch. Pharm. 73, 91; Mendius (1862), Ann. Ch. Pharm. 121, 129; Hofmann (1882), Ber. 14, 2725 and (1883) Ber. 15, 407 and 762; Tafel (1886), Ber. 19, 1924.

20 grms. acetamide.
54 „ bromine.
56 „ caustic potash.

A 10 per cent. solution of caustic potash (about 20 grms.) is added in the cold to 20 grms. acetamide, previously dissolved in 54 grms. bromine, until the dark brown liquid changes to a deep yellow colour. The solution, which now contains potassium bromide and acetmonobromamide, is slowly added from a tap-funnel inserted, together with a thermometer,

into the tubulus of a retort ($\frac{1}{2}$ litre capacity) which contains a concentrated solution of 56 grms. caustic potash heated to 60—70°. Heat is evolved, and care must be taken that the rise of temperature does not greatly exceed the above limits. The reaction goes on quietly, and the yellow solution is gradually decolourised. The mixture is then digested for a short time at the above temperature until the yellow colour completely disappears, and the liquid distilled with a naked flame. The vapours of methylamine and ammonia which are evolved are passed into dilute hydrochloric acid contained in the receiver. When the methylamine has been driven over, the hydrochloric acid solution is evaporated to dryness on the water-bath, and the colourless crystalline residue extracted repeatedly with small quantities of absolute alcohol, which dissolves out the methylamine salt from the ammonium chloride. From the hot alcoholic solution foliated crystals separate out on cooling.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + 2Br + KOH = \underset{\text{Acetmonobromamide.}}{CH_3.CONHBr} + KBr + H_2O$$

$$CH_3CONHBr + KOH = CN_3CON + KBr + H_2O$$

$$\underset{\text{Methyl Carbimide}}{CH_3.N:C:O} + H_2O = \underset{\text{Methylamine.}}{CH_3NH_2} + CO_2$$

Properties.—Large deliquescent tablets, which melt at 200°, and sublime above 220° with slight decomposition. The base is liberated, on warming with caustic soda, as an inflammable gas.

PREPARATION LX.

(1.)

ETHYL ACETATE, $C_4H_8O_2 = CH_3,CO_2C_2H_5$.
(*Acetic Ether.*)

LITERATURE.—Frankland, Duppa (1865), Phil. Trans. 156, 37; Eghis (1873), Ber. 6, 1177; Pabst (1880), Bull. Soc. Chim. 33, 350.

100 grms. sodium acetate (fused).
60 ,, alcohol (absolute).
150 ,, conc. sulphuric acid.

One hundred grms. fused and coarsely powdered sodium acetate are slowly added to a cooled mixture of 60 grms. alcohol (absolute) and 150 grms. conc. sulphuric acid contained in a round-bottomed flask of about ½ litre capacity and connected with a condenser and receiver. After standing about two hours the produce is distilled first on the water-bath and finally over the naked flame. The ethyl acetate is separated from the distillate, which contains in addition, acetic acid, alcohol, ether and sulphurous acid, by shaking up with a concentrated solution of soda or brine. The upper layer of liquid is removed, dehydrated over calcium chloride and distilled on the water-bath. The portion distilling below 74° contains

ether, that boiling at 74—79°, which is principally ethyl acetate, is separately collected and purified by redistillation.

$$2CH_3.COONa + 2C_2H_5OH + H_2SO_4 = \underset{\text{Ethyl Acetate.}}{2CH_3.CO_2C_2H_5} + Na_2SO_4 + 2H_2O$$
Sodium Acetate

(2.)

50 c.c. conc. sulphuric acid.
50 „ alcohol (absolute).
Mixture of equal volumes of glacial acetic acid and absolute alcohol.

A mixture of 50 c.c. conc. sulphuric acid and 50 c.c. absolute alcohol contained in a round-bottomed flask of about ½ litre capacity and connected with condenser and receiver is heated to 130° and a mixture of equal volumes of glacial acetic acid and absolute alcohol is slowly added from a tap funnel in a continuous stream at such a rate that the contents of the flask are maintained at a constant temperature of 130°. Acetic ether and water distil over into the receiver and are purified by the method given above.

$$C_2H_5(OH) + H_2SO_4 = \underset{\text{Ethyl Sulphate.}}{C_2H_5SO_4H} + H_2O$$

$$C_2H_5SO_4H + CH_3CO_2H = \underset{\text{Ethyl Acetate.}}{C_2H_5O_2C.CH_3} + H_2SO_4$$

Properties.—Colourless liquid, possessing an agreeable smell; b. p. 77°; sp. gr. ·9068 at 15°; soluble in about 11 parts water, miscible in all proportions with alcohol, ether, and acetic acid.

PREPARATION LXI.

ETHYL ACETOACETATE, $C_6H_{10}O_3$ = $CH_3.CO.CH_2.COOC_2H_5$.
(*Acetoacetic Ethyl Ester.*)

LITERATURE.—Geuther (1863), Jahresb. 323; Frankland, Duppa (1865), Phil. Trans. 156, 37; Wislicenus (1877), Ann. Ch. Pharm. 186, 161.

200 grms. ethyl acetate.
20 ,, sodium.

Two hundred grms. ethyl acetate, carefully dehydrated over calcium chloride, are introduced into a dry flask of about ½ litre capacity connected with a long and well cooled condenser. 20 grms. well pressed sodium cut into thin pieces are quickly added and the flask cooled. A brisk reaction sets in and the liquid boils. When the first action is over and no further evolution of heat occurs, the mixture is heated on the water-bath with a condenser until the sodium is completely dissolved. The excess of acetic ether is now distilled off in the water-bath and to the warm

residual liquid 100 grms. 50 per cent. acetic acid is added and the whole well shaken. On cooling 100 grms. water are added and the mixture again well stirred. The liquid divides into two layers; the upper one, consisting of acetoacetic ester, is drawn off and the aqueous layer is extracted with ether, from which, on evaporating off the ether, a further quantity of acetoacetic ester may be obtained. The united portions are washed with a small quantity of water, the aqueous layer separated and the product fractionated in 5 fractions[1] (100—130°, 130—135°, 165—175°, 175—185° 185—200°). The fraction distilling at 175—185° is nearly pure acetoacetic ester. The brown residue remaining in the distilling flask solidifies on cooling to a crystalline mass consisting chiefly of dehydracetic acid, $C_8H_8O_4$. It is converted into the sodium salt by boiling with soda solution with the addition of animal charcoal and the latter crystallised. On adding dilute sulphuric acid the free acid is obtained nearly pure (colourless needles; m. p. 109°; b. p. 279·6°.)

$$\underset{\text{Acetic Ester}}{2CH_3COOC_2H_5} + 2Na = \underset{\text{Sodium Acetoacetic Ester.}}{CH_3CO.CHNa.COOC_2H_5} + C_2H_5ONa + 2H$$

$$CH_3COCHNaCO_2C_2H_5 + CH_3CO_2H = \underset{\text{Acetoacetic Ester.}}{CH_3.CO.CH_2.CO_2C_2H_5} + CH_3CO_2Na$$

Properties.—Colourless liquid possessing a fruity odour; b. p. 182°; sp. gr. 1.03 at 5°; very slightly

[1] A better method is to fractionate the ester in vacuō (see Fig. 19) using a distilling flask and condenser.

soluble in water. Ferric chloride gives a violet coloration. Boiled with caustic soda solution the ether splits up into alcohol, carbon dioxide, acetone, and, in smaller quantity, acetic acid.

PREPARATION LXII.

ETHYL ACETOSUCCINATE, $C_{10}H_{16}O_5$ = $CH_3.CO.CH.CO_2C_2H_5$. $CH_2.CO_2C_2H_5$.

LITERATURE.—Conrad (1877), Ann. Ch. Pharm. 188, 215; Rach (1886), Ann. Ch. Pharm. 234, 36.

52 grms. ethyl acetacetate.
9·2 „ sodium.
150 „ absolute alcohol.
125 „ ethyl monochloracetate.

9·2 grms. metallic sodium in thin slices are dissolved in 150 grms., absolute alcohol contained in a round-bottom flask connected with a reflux condenser. When the first reaction is over, any undissolved sodium may be brought into solution by heating for a short time on the water-bath. 52 grms. ethyl acetacetate are gradually added to the cold alcoholic

solution of sodium ethylate, the mixture being kept cool. The liquid changes to a faint amber colour. The calculated quantity (125 grms.) of ethyl monochloracetate is now slowly introduced, the flask being cooled in water if much heat is developed. The reaction is completed by heating for two hours on the water-bath. The liquid becomes gradually muddy from the separation of sodium chloride and assumes a brown tint. If the reaction is finished a sample of the product diluted with water should no longer have an alkaline reaction. After distilling off the alcohol the residual dark-coloured product is diluted with water and the oily liquid which settles down (ethyl acetosuccinate) is separated, dried over previously heated potassium carbonate and then distilled, whereby the chief portion passes over at 250–260° and is nearly pure ethyl acetosuccinate. It usually has a faint yellow colour.

$$\underset{\text{Sodium Ethylacetacetate}}{CH_3.CO.CHNa.CO_2C_2H_5} + \underset{\text{Chloracetic Ester.}}{CH_2Cl.CO_2C_2H_5} =$$

$$CH_3.CO.\underset{\displaystyle CH_2\ CO_2C_2H_5}{\overset{\displaystyle CH.CO_2C_2H_5}{\overset{|}{\underset{|}{\ }}}} + NaCl$$

Ethyl Acetosuccinate.

Properties.—Colourless liquid; b. p. 254–256°; sp. gr. 1·079 at 21°; insoluble in water; soluble in alcohol.

PREPARATION LXIII.

MONOCHLORACETIC ACID, $C_2H_3O_2Cl = CH_2Cl{\cdot}CO_2H$.

LITERATURE.—R. Hofmann (1857), Ann. Ch. Pharm. 102, 1; H. Müller (1865), Chem. Soc. J. 17, 398.

150 grms. glacial acetic acid.
12 ,, red phosphorus.

One hundred and fifty grms. glacial acetic acid and 12 grms. red phosphorus are heated in a retort of about ½ litre capacity provided with a reflux condenser on a water-bath and chlorine, dried through sulphuric acid, is passed into the hot liquid.* The operation must be conducted in such a way that the chlorine comes in contact as much as possible with the vapours of the hot acid. This is effected by fixing the chlorine inlet tube just below the surface of the liquid. At the upper end of the condenser quantities of unabsorbed chlorine and hydrochloric acid gas escape. The retort is placed in direct sunlight, the action proceeding more or less quickly according to the strength of the sun's rays. In direct sunlight the greater part of the acetic acid is converted into the monochlorinated compound in 6—8 hours. The action slackens as the formation of the chloracetic acid proceeds. The yellow product is distilled with the thermometer in the liquid; the portion distilling below 130° consists chiefly of unchanged acetic acid and may be used for a fresh operation, that boiling at 130—190° contains

nearly the whole of the monochloracetic acid, the portion which boils above 190° consists of higher chlorinated products (di- and trichloracetic acid). The fraction boiling at 130—190° quickly solidifies on cooling. The colourless crystalline plates are separated from the mother liquor by pressing them well at the filter pump and are dried *in vacuo* over sulphuric acid and caustic potash. On redistilling the monochloracetic acid, thus purified, it passes over at 184—188°.

$$\underset{\text{Acetic Acid}}{CH_3CO_2H} + 2Cl = \underset{\text{Monochloracetic Acid.}}{CH_2Cl.CO_2H} + HCl$$

Properties.—Rhombic plates or prisms; m. p. 63°; b. p. 185—187°; easily soluble in water.

PREPARATION LXIV.

GLYCOCOLL, $C_2H_5NO_2 = CH_2\begin{cases}NH_2\\CO.OH.\end{cases}$

(*Amidoacetic Acid.*)

LITERATURE.—Braconnot (1820), Ann. Ch. Phys. (2) 13, 114; Dessaignes (1846), Ann. Ch. Phys. (3) 17, 50; Strecker (1848), Ann. Ch. Pharm. 65, 130; Perkin, Duppa (1859), Chem. Soc. J. 11, 22; Nencki (1883), Ber. 16, 2827.

50 grms. monochloracetic acid.

150 „ ammonium carbonate (commercial).

Fifty grms. monochloracetic acid are well mixed with 150 grms. dry powdered commercial ammonium carbonate, and the mixture slowly heated in an open

flask (1 litre capacity) on the oil-bath. At 60—70° the action begins, the mass melts and froths up with strong evolution of carbon dioxide. As the temperature slowly rises to 130° the evolution of gas slackens, and the contents of the flask, which have a faint brown tint, become semi-solid, from the separation of ammonium chloride. The lamp is now removed, the cooled mass dissolved in water and the aqueous solution boiled with lead oxide until the smell of ammonia is no longer perceptible. From the warm filtered solution lead is precipitated with sulphuretted hydrogen and the filtrate is now heated with copper carbonate. The deep blue liquid filtered from excess of carbonate is concentrated. On cooling, the characteristic blue crystals of the copper salt of glycocoll separate out. These are filtered, drained, redissolved in water, and the copper precipitated with sulphuretted hydrogen. The clear solution, evaporated on the water-bath, yields colourless crystals of free glycocoll.

$$\underset{\text{Chloracetic Acid}}{CH_2Cl.COOH} + (NH_4)_2CO_3 = \underset{\text{Glycocoll.}}{CH_2\overset{NH_2}{\underset{CO_2H}{}}} + CO_2 + H_2O + \underset{}{NH_4Cl}$$

Properties.—Large monoclinic crystals, are discoloured at 228° and melt at 232-236°; scarcely soluble in alcohol and ether, readily soluble in water (1 part glycocoll in 4 parts water). The aqueous solution gives a deep red colour with ferric chloride.

PREPARATION LXV.

ETHYL MONOCHLORACETATE, $C_4H_7O_2Cl$ = $CH_2Cl.CO_2C_2H_5$.
(*Monochloracetic Ester.*)

LITERATURE.—Willm (1857), Ann. Ch. Phys. (3) 49, 97; Conrad (1877), Ann. Ch. Pharm. 188, 218.

200 grms. monochloracetic acid.
120 „ absolute alcohol.
25 „ conc. sulphuric acid.

A mixture of 200 grms. monochloracetic acid, 120 grms. absolute alcohol, and 25 grms. conc. sulphuric acid, is heated for about six hours on the water-bath in a round-bottomed flask, of about $\frac{1}{2}$ litre capacity, connected with a reflux condenser. On the addition of water to the product of the reaction, previously allowed to cool, the ester separates out. The ethereal layer is removed, dehyrated over calcium chloride, and distilled. The portion passing over at 138—145°, is collected, and after fractionation boils constantly at 143—144°.

$$\underset{\text{Chloracetic Acid}}{CH_2ClCO_2H} + C_2H_5(OH) = \underset{\text{Ethylchloracetic Ester.}}{CH_2Cl.CO_2C_2H_5} + H_2O$$

Properties.—Colourless liquid, possessing an ethereal dour; b. p. 143·5°; sp. gr. 1·1585 at 20°.

PREPARATION LXVI.

DIETHYL MALONATE, $C_7H_{12}O_4 = CH_2\langle^{CO_2C_2H_5}_{CO_2C_2H_5}$.

LITERATURE.—Conrad (1880), Ann. Ch. Pharm. 204, 126; Venable (1880), Ber. 13, 1651; Claisen, Crismer (1883), Ann. Ch. Pharm. 218, 131.

100 grms. monochloracetic acid.
200 „ water.
75 „ potassium carbonate.
75 „ potassium cyanide.

One hundred grms. monochloracetic acid are dissolved in 200 grms. water in a porcelain basin, and the solution neutralised with 75 grms. potassium carbonate.* Seventy-five grms. powdered potassium cyanide are now added, and the mixture heated on the sand-bath until the reaction sets in with strong ebullition. When the reaction is over, the contents of the basin are evaporated as rapidly as possible on the sand-bath, with constant stirring, until a thermometer inserted into the brown semi-fluid mass indicates a temperature of 135°. The mass is allowed to cool without interrupting the stirring and, when cold, the hard saline deposit, consisting of potassium

chloride and potassium cyanacetate is finely powdered and introduced into a round-bottomed flask connected with a condenser. Two-thirds the weight of absolute alcohol is added and the mixture, heated on the water-bath, is saturated with dry hydrochloric acid gas.* The gas is conducted in through a funnel or wide adapter to prevent the inlet tube becoming choked with the crystalline precipitate which is formed. When hydrochloric acid has been passed in for about ten hours, the contents of the flask are cooled, poured into ice water and shaken with 300 c.c. commercial ether, in which the ethyl malonate dissolves. The ethereal layer is then separated from the acid liquid and washed with water and potassium carbonate solution, drawn off, dehydrated over calcium chloride and distilled. When the ether has been driven off, the greater portion of the residue distils at 190—200°. After one or two fractionations the ester is found to boil at 195—196° and is pure.

$$\underset{\text{Monochloracetic Acid}}{CH_2Cl.CO_2H} + KCN = \underset{\text{Cyanacetic Acid.}}{CH_2CN.CO_2H} + KCl$$

$$CH_2{\overset{CN}{\underset{COOH}{}}} + 2C_2H_5OH + HCl = \underset{\text{Diethyl Malonate.}}{CH_2{\overset{CO_2C_2H_5}{\underset{CO_2C_2H_5}{}}}} + NH_4Cl$$

Properties.—Colourless liquid; b. p. 195°; sp. gr. 1·068 at 18°; insoluble in water.

PREPARATION LXVII.

ETHYLMALONIC ACID, $C_5H_8O_4 = C_2H_5CH\langle^{CO_2H}_{CO_2H}$

LITERATURE.—Wislicenus, Urech (1873), Ann. Ch. Pharm. 165, 93; Tupolew (1874), Ann. Ch. Pharm. 171, 243; Markownikow, Ann. Ch. Pharm. 182, 329; Conrad (1880), Ann. Ch. Pharm. 204, 134.

16 grms. ethyl malonate
25 „ absolute alcohol.
2.3 „ sodium.
20 „ ethyl iodide.

Sodium ethylate is first prepared by dissolving 2.3 grms. sodium in 25 grms. absolute alcohol, and the reaction completed, if necessary, on the water-bath as described on p. 132. Whilst the product is still slightly warm, 16 grms. malonic ether are added from a tap funnel. The liquid remains clear at first, but before the ether has all been added a white crystalline body (sodium ethyl malonate) separates out, and soon the whole solidifies. To the solid mass 20 grms. ethyl iodide are slowly added. The mass softens, and after continued shaking completely liquefies with evolution of heat. The product is now heated on the water-bath, when it becomes turbid from the separation of sodium iodide in the form of a fine powder.

After 1½ hours the liquid ceases to be alkaline, and the reaction is complete. The alcohol is distilled off on a brine-bath. On the addition of water an almost colourless oil separates out. The oil is separated by extraction with ether dehydrated over calcium chloride and distilled. When the ether has been driven off, almost the whole of the residue (ethyl diethyl-malonate) passes over at 206—208°.

Properties.—Colourless liquid, with an agreeable fruity smell; b. p. 207°, sp. gr. 1·008 at 18°.

To obtain the free acid, the ester is saponified with caustic potash. To 25 grms. caustic potash in strong aqueous solution the ether is slowly added from a tap funnel. At first an emulsion forms, which soon solidifies to a white mass. This is heated on the water-bath with constant shaking for about three quarters of an hour, until it becomes completely liquid. The saponification is then complete. The product is diluted with water, neutralised with hydrochloric acid, and the free acid precipitated with calcium chloride as the calcium salt. This is separated from the solution by filtration and concentrated hydrochloric acid added. From the acid solution the free ethylmalonic acid is extracted by shaking with ether. After evaporating off the ether, the acid remains behind as a syrup, which solidifies when cold. This is redissolved in water, boiled with a little animal charcoal to free it from any adhering colouring matter,

filtered and evaporated to syrupy consistency on the water-bath. The colourless acid crystallises on cooling.

$$\underset{\text{Sodium Ethyl Malonate}}{CHNa(CO_2C_2H_5)_2} + C_2H_5I = \underset{\text{Ethyl Diethyl Malonate.}}{C_2H_5CH(CO_2C_2H_5)_2} + NaI$$

$$C_2H_5CH(CO_2C_2H_5)_2 + 2KOH = \underset{\text{Potassium Ethyl Malonate.}}{C_2H_5CH(CO_2K)_2} + 2C_2H_5OH$$

Properties.—Rhombic prisms; m. p. 111·5°, easily soluble in water, alcohol and ether; decomposes completely at 160° into carbon dioxide and butyric acid.

PREPARATION LXVIII.

TRICHLORACETIC ACID, $C_2HCl_3O_2 = CCl_3CO_2H$.

LITERATURE.—Dumas (1838), Compt. rend. 8, 609; Kolbe (1844), Ann. Ch. Pharm. 49, 341 and (1845) Ann. Ch. Pharm. 54, 183; Judson (1870), Chem. Soc. J. 24, 232; Clermont (1871), Compt. rend. 73, 113; (1872) 74, 1492; (1874) 76, 774.

100 grms. chloral hydrate.
40 „ fuming nitric acid, sp. gr. 1·5.

In a flask of 500 c.c. capacity 100 grms. commercial chloral-hydrate are heated to melting, and 40 grms. fuming nitric acid are added to the melted mass.* The mixture is heated carefully over a small flame until the reaction sets in. After a few minutes red fumes

are evolved; the reaction proceeds without the application of heat, and is complete when, on warming the liquid, nitrous fumes cease to come off. The product is now distilled; below 123° excess of nitric acid distils; between 123° and 194° a mixture of trichloracetic acid and a small quantity of nitric acid pass over, and at 194—196° nearly pure trichloracetic acid collects in the receiver and solidifies on cooling. The fraction boiling at 123—190° is treated with a fresh quantity of fuming nitric acid, and the product purified as above.

$$\underset{\text{Chloral}}{CCl_3.CHO} + O = \underset{\text{Trichloracetic Acid.}}{CCl_3.CO_2H}$$

Properties. — Colourless, rhombohedral crystals; m. p. 55°; b. p. 195°.

PREPARATION LXIX.

DIETHYL OXALATE, $C_6H_{10}O_4 = \frac{CO_2C_2H_5}{CO_2C_2H_5}$

(*Oxalic Ester.*)

LITERATURE.—Frankland, Duppa; Fittig (1886), Grundr. der Org. Chem. 253.

210 grms. anhydrous oxalic acid.
140 „ absolute alcohol.

A mixture of 210 grms. oxalic acid dehydrated at 100° and 140 grms. absolute alcohol is slowly heated to 100° in a flask of about ¾ litre capacity connected with a condenser and receiver. The vapour of 140 grms. of a further quantity of absolute alcohol contained in a second flask is passed into the bottom of first flask, in a continuous, but not too rapid stream, the temperature of the contents of the latter being gradually raised to 125—130°. The liquid, which distils, consists of water, alcohol, and a small quantity of oxalic ether, and may be used for the preparation of oxamide. The latter on the addition of conc. aqueous ammonia is precipitated in the form of a white crystalline powder, $C_2O_2(NH_2)_2$. The contents of the flask are now distilled, and the colourless liquid which passes over at 182—186° collected in a separate vessel.

$$\underset{\text{Oxalic Acid}}{C_2H_2O_4} + 2C_2H_5OH = \underset{\text{Diethyl Oxalate}}{C_2O_4(C_2H_5)_2} + 2H_2O$$

Properties.—Colourless liquid; b. p. 186°; sp. gr. 1·103 at 0°; easily soluble in alcohol and ether; not miscible with water.

PREPARATION LXX.

ETHYL DIETHYL-OXYACETATE, $C_8H_{16}O_3$ =

$$(C_2H_5)_2C\begin{matrix}OH\\ CO_2C_2H_5\end{matrix}$$

(*Ethyl Diethoxalate.*)

LITERATURE.—Frankland, Duppa (1865), Proc. Roy. Soc. 12, 396; 14, 17; Geuther, Wackenroder (1867), Zeitschcr. f. Ch. N. F. 3, 709; Fittig, Howe (1880), Ann. Ch. Pharm. 200, 21.

50 grms. ethyl oxalate.
107 „ ethyl iodide.
granulated zinc.

Fifty grms. oxalic ester are mixed with 107 grms. ethyl iodide in a round-bottomed flask of ½ litre capacity, and so much granulated zinc (dried at 100°, and slightly amalgamated by dipping it into a weak solution of corrosive sublimate) added, that it remains just covered by liquid. The mixture is heated with reflux condenser on the water-bath for 12—15 hours to 50—60°, when the liquid, which at the beginning is clear and of a light yellow colour solidifies to a yellowish-brown semi-crystalline mass. If water be now added to the product until its volume is three times that of the crystalline mass, a strong evolution of gas (ethane) occurs, and the ethyl ester separates out as an oil together with the

unattacked ethyl iodide and is distilled (in a copper vessel) with steam. The distillate is purified by fractional distillation. When the ethyl iodide and alcohol have distilled, the thermometer rises rapidly to 165°, and the portion passing over between 165° and 180° is collected separately. By repeatedly distilling this fraction the ethereal salt of diethyl oxalic acid is obtained pure.

$$\begin{matrix}CO_2C_2H_5\\ CO_2C_2H_5\end{matrix} + 2Zn + 2C_2H_5I = \begin{matrix}(C_2H_5)_2CO.ZnC_2H_5\\ CO_2C_2H_5\end{matrix} + ZnI_2$$

Ethyl Oxalate

$$\begin{matrix}(C_2H_5)_2.COZnC_2H_5\\ CO_2C_2H_5\end{matrix} + H_2O = (C_2H_5)_2C\begin{matrix}(OH)\\ CO_2C_2H_5\end{matrix} + ZnO + C_2H_6$$

Ethyl Diethyl-Oxyacetate.

Properties.—Colourless liquid; b. p. 175°: sp. gr. ·9896 at 16·5°.

PREPARATION LXXI.

FORMIC ACID, $CH_2O_2 = H.CO_2H$.

LITERATURE.—Berthelot (1856), Ann. Ch. Phys. (3) 46, 477; Lorin (1866), Bull. soc. chim. (2) 5, 7; (1870) (2) 14, 367.

50 grms. anhydrous glycerin.
150 „ oxalic acid.

Fifty grms. commercial crystallised oxalic acid and 50 grms. glycerin dehydrated at 175° are

heated in a retort of ¼-litre capacity with condenser and receiver over wire gauze. The reaction begins at 75°, and at 90° proceeds briskly; carbonic anhydride is evolved and aqueous formic acid distils. When the temperature has been maintained for some time at 90—105° and the evolution of carbonic anhydride has nearly ceased, the contents of the retort are cooled to about 80°, and a further 50 grms. crystallised oxalic acid added. The reaction recommences with the formation of aqueous formic acid, which, however, becomes more concentrated with each fresh addition of oxalic acid until the distillate contains 56 per cent. of the acid. In order to regain the formic acid, which remains as monoformin in the retort, the contents are diluted with about ½ litre water and distilled in a current of steam until the distillate has only a faintly acid reaction. On neutralising the united acid distillates by boiling with excess of lead carbonate and concentrating the filtered solution, the lead salt of formic acid is obtained in long colourless prisms, which decompose with sulphuretted hydrogen yielding the anhydrous acid. The powdered salt well dried at 100—110° is introduced in a long layer into the inner tube of a condenser loosely stopped at the lower end by a plug of glass wool, or asbestos.* To the end of the condenser a receiver is attached, which is guarded from moisture by a drying tube. The salt is heated gently by moving a flame along the tube or by

passing steam into the outer tube of the condenser. Sulphuretted hydrogen washed through water and

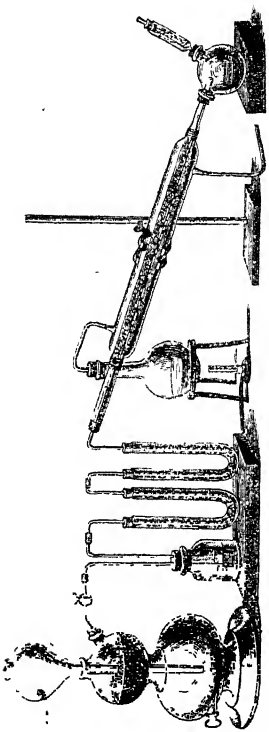


FIG. 30.

then dried by passing over calcium chloride is led over the salt in not too rapid a stream. The arrange-

ment of the apparatus is shown in Fig. 30. The lead formate blackens, and is slowly converted into lead sulphide and formic acid, which flows down into the receiver. The acid, which retains a strong smell of sulphuretted hydrogen, dissolved in the acid is freed from the latter by a second distillation over dry lead formate.

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Oxalic Acid}}{C_2H_2O_4} = \underset{\text{Monoformin.}}{C_3H_5{\overset{(OH)_2}{O.COH}}} + CO_2 + H_2O$$

$$C_3H_5{\overset{(OH)_2}{O.COH}} + H_2O = \underset{\text{Formic Acid.}}{HCO_2H} + C_3H_5(OH)_3$$

Properties.—Colourless liquid with a penetrating smell; b. p. 99°; sp. gr. 1·223 at 0°; solidifies below 0° to colourless crystals; m. p. 8·6°; soluble in water and alcohol; decomposes on heating with silver and mercury salts, the metals being deposited.

PREPARATION LXXII.

ALLYL ALCOHOL, $C_3H_6O = CH_2 : CH.CH_2OH$

LITERATURE.—Cahours, Hofmann (1857), Ann. Ch. Pharm. 102, 285; Tollens, Henninger (1870), Ann. Ch. Pharm. 156, 129.

50 grms. oxalic acid.
200 „ glycerin.
¼ „ ammonium chloride.

A mixture of 50 grms. commercial powdered oxalic acid, 200 grms. commercial glycerin, and $\frac{1}{4}$ grm. salammoniac, are heated in a retort of about $\frac{1}{2}$ litre capacity over wire gauze with a Bunsen lamp.* Strong evolution of carbonic acid gas at first occurs, and the temperature, indicated by a thermometer inserted into the retort, remains for some time stationary at about 130°. As the temperature slowly rises, the evolution of gas slackens, and after a time (at about 180°) entirely ceases. When the temperature has reached 195° the receiver, which now contains aqueous formic acid, is changed. At 200—210° carbonic acid is again given off, and oily streaks are observed to run down the neck of the retort; at the same time a disagreeable penetrating smell is perceptible. By gently heating the contents of the retort, a temperature of 220—230° is maintained for some time, and when it has finally risen to 260° the distillation is stopped. The distillate is a mixture of allyl alcohol and water, and there is also present allyl formate, glycerin, and acrolein. Excess of glycerin remains behind in the retort, and may be used again by repeating the operation with a smaller quantity of oxalic acid (30—40 grms.) until the residue is too small or has become dark-coloured and thick. The whole of the allyl alcohol, together with a small quantity of formic acid, and acrolein, is obtained by submitting the distillate to a second distillation. The distillation

is this time continued until on treating the last portions with potassium carbonate no oily layer (usually of a faint yellow colour) separates. This occurs at about 105°. On adding solid potassium carbonate to the distillate, the allyl alcohol settles out as an oil. This is drawn off, and 5—10 per cent. powdered caustic potash added. After having been allowed to stand for twenty-four hours and well shaken or gently warmed for a short time, the liquid loses the smell of acrolein and at the same time assumes a brown colour. In order to abstract the last traces of water, which are obstinately retained, the allyl alcohol is left in contact with anhydrous baryta and then distilled.

$$\underset{\text{Oxalic Acid}}{C_2H_2O_4} + \underset{\text{Glycerin}}{C_3H_8O_3} = C_3H_7O_2.O_2CH + H_2O + CO_2$$

$$C_3H_7O_2.O_2CH = \underset{\text{Allyl Alcohol.}}{C_3H_5OH} + H_2O + CO_2$$

Properties. — Colourless liquid with a pungent odour; b. p. 96°; sp. gr. 0·858 at 0°.

PREPARATION LXXIII.

ALLYL IODIDE, $C_3H_5I = CH_2 : CH.CH_2I$.

LITERATURE.—Berthelot, de Luca (1855), Ann. Ch. Phys. (3) 43, 257; Tollens, Henninger (1870), Ann. Ch. Pharm. 156, 156; Saytzew, Kanonikoff (1877), Ann. Ch. Pharm. 185, 191; Wagner (1876), Ber. 9, 1810.

100 grms. anhydrous glycerin.
70 „ iodine.
23 „ yellow phosphorus.

Through a mixture of 100 grms. glycerin dehydrated at 175°, and 70 grms. dry powdered iodine, contained in a retort of about ½-litre capacity and connected with condenser and receiver, a slow current of dry carbonic acid is passed.* 23 grms. yellow phosphorus cut into pieces about the size of a pea and dried between filter-paper are gradually added. The action is assisted at first by gently warming the retort with a small flame. A rather violent reaction then sets in, which is maintained by the addition of more phosphorus, and must be so regulated that the allyl iodide distils as it is produced; otherwise isopropyl iodide is formed. The distillate divides into two layers, and is coloured by dissolved iodine, which has been carried over. The lower layer is washed with dilute caustic soda solution and with water, and is separated from the aqueous portion by a tap-funnel. After dehydrating the liquid over calcium chloride it is distilled. The portion passing over at 98—102° is nearly pure allyl iodide and may be used for further experiments.

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + I + P = \underset{\text{Allyl Iodide.}}{C_3H_5I} + P(OH)_3$$

Properties.—Colourless liquid with an alliaceous odour; b. p. 101—102°; sp. gr. 1·789 at 16.°

PREPARATION LXXIV.

*Propenyl Tribromide, $C_3H_5Br_3$ = $CH_2Br.CHBr.CH_2Br$.
(*Tribromhydrin.*)

LITERATURE.—Berthelot (1856), Ann. Ch. Phys. (3) 48, 304; Wurtz (1857), Ann. Ch. Phys. (3) 51, 91; Henry (1870), Compt. rend. 70, 638; Tollens (1870), Ann. Ch. Pharm. 156, 168.

50 grms. allyl iodide.
75 ,, bromine.

Seventy-five grms. bromine are slowly added in small portions at a time to 50 grms. allyl iodide contained in a flask, which is connected with an air condenser and well cooled in a freezing mixture.* The liquid is then allowed to stand twenty-four hours and separated by filtration from the iodine, which has meanwhile crystallised out. The brown filtrate is repeatedly washed with dilute caustic soda solution and then with water. The allyl bromide is separated from the aqueous portion, dehydrated over fused calcium chloride and distilled. The colour of the liquid on boiling changes to a dark brown and iodine vapours are given off abundantly. The distillate is again treated with caustic soda and water, &c., and redistilled. The temperature, indicated by the thermometer, rises rapidly to 180° and the greater portion of the liquid

distils at 200—220°. This fraction crystallises on standing for a time in a freezing mixture and the crystals are separated from the mother liquor by decantation. The product is purified by repeated distillations.

$$\underset{\text{Allyl Iodide}}{C_3H_5I} + Br_2 = \underset{\text{Allyl Tribromide}}{C_3H_5Br_3} + I$$

Properties.— Colourless glistening prisms; m. p. 16°, b. p. 219—220°.

PREPARATION LXXV.

TRICARBALLYLIC ACID, $C_6H_8O_6 = \begin{matrix} CH_2.COOH. \\ CH.COOH. \\ CH_2.COOH. \end{matrix}$

(*Propenyl-tricarboxylic Acid.*)

LITERATURE.—Simpson (1865), Proc. Roy. Soc. 14, 77.

50 grms. propenyl tribromide.
36 „ potassium cyanide.

Fifty grms. allyl bromide are dissolved in excess of alcohol and 36 grms. coarsely powdered potassium cyanide added. The whole is then heated in a soda-water bottle with the cork well tied down for 15 hours in the water-bath. The bottle is well cooled and carefully opened and the alcoholic liquid filtered from the potassium bromide, which has separated out. The filtrate is now heated with reflux condenser on the

water-bath with a sufficient quantity of caustic potash (40 grms.) to decompose the cyanide formed, until the evolution of ammonia gas has ceased. The alcohol is distilled off on the brine-bath and an excess of nitric acid added to the cooled residue. On evaporating the mass on the water-bath a residue consisting of potassium nitrate and free tricarballylic acid remain from which, after being well dried and powdered, the latter may be extracted with absolute alcohol. On evaporating off the alcohol, the acid remains as a dark-coloured substance and is purified by recrystallisation from water with the addition of animal charcoal.

$$\underset{\text{Propenyl Tribromide}}{C_3H_5Br_3} + 3KCN = \underset{\text{Propenyl Tricyanide.}}{C_3H_5(CN)_3} + 3KBr$$

$$C_3H_5(CN)_3 + 3KOH + 3H_2O = \underset{\text{Potassium Tricycarballylate.}}{C_3H_5(COOK)_3} + 3NH_3$$

Properties.—Colourless rhombic plates; m. p. 158°; easily soluble in water and alcohol.

PREPARATION LXXVI.

GLYCERIC ACID, $C_3H_6O_4 = CH_2(OH).CH(OH).CO_2H$ (*Dioxypropionic Acid.*)

LITERATURE.—Debus (1858), Ann. Ch. Pharm. 106, 79; Sokolow (1858), Ann. Ch. Pharm. 106, 95; Beilstein (1861), Ann. Ch. Pharm. 120, 226; Mulder (1876), Ber. 9, 1902.

50 grms. glycerin.
50 ,, fuming nitric acid, sp. gr. 1·5.

Fifty grms. glycerin diluted with an equal volume of water are introduced into a tall narrow glass cylinder. 50 grms. fuming nitric acid sp. gr. 1·5 are carefully run in below the surface of the glycerin by means of a funnel (the neck of which is drawn out into a fine tube) so that two layers are formed. The cylinder is left at the ordinary temperature for some little time until the two layers have diffused and formed a homogeneous liquid. The contents of several such cylinders are slowly evaporated on the water-bath to a syrupy consistence. The residue is diluted with about 2 litres of water and the aqueous solution of glyceric acid neutralised with lead carbonate and a small quantity of lead oxide. Towards the end of the operation the liquid is heated to boiling and filtered whilst hot. On concentrating and cooling the aqueous solution, the impure lead salt of glyceric acid is obtained, which may be purified by recrystallisation. The salt which crystallises out in crusts on the sides of the vessel to which it firmly adheres, may be detached by warming. By concentrating the mother liquors a further quantity of crystals slowly separates out. The finely powdered salt is mixed into a paste with water and decomposed in portions of 25 grms. with sulphuretted hydrogen.

The aqueous solution, filtered from lead sulphide, is evaporated on the water-bath, when the acid remains in the form of a thick syrup.

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + O_2 = \underset{\text{Glyceric Acid.}}{C_3H_6O_4} + H_2O$$

Properties.—Strongly acid syrup of a faint yellow colour, which does not crystallise; soluble in water and alcohol, insoluble in ether.

PREPARATION LXXVII.

β-IODPROPIONIC ACID, $C_3H_5IO_2 = CH_2I.CH_2.COOH$.

LITERATURE.—Beilstein (1861), Ann. Ch. Pharm. 120, 230 and (1862) 122, 366; Moldenhauer (1864), Ann. Ch. Pharm. 131, 323; Kekulé (1864), Ann. Ch. Pharm. 131, 223; Mulder (1876), Ber. 9, 1902; Wislicenus (1873), Ann. Ch. Pharm. 166, 1; Erlenmeyer (1878), Ann. Ch. Pharm. 191, 284.

52 c.c. glyceric acid sp. gr. 1·26.
100 grms. phosphorus diiodide.

One hundred grms. phosphorus diiodide[1] are added in small quantities to 52 c.c. glyceric acid sp. gr. 1·26 contained in a large round-bottomed flask and in order

[1] *Preparation of Phosphorus Diiodide* (Fittig (1886), *Grundriss der Org. Chem.*).—Forty-one parts dry powdered iodine are added to a well-cooled solution of 5 parts phosphorus dissolved in carbon bisulphide. The carbon bisulphide is then distilled off.

to start the process the mixture is gently heated. A violent reaction sets in with the formation of a dark brown syrupy liquid. If the reaction proceeds too violently the flask is cooled in water. The product is again heated, when a second less violent reaction occurs and a light yellow liquid is produced, which on cooling solidifies to a crystalline mass. From this, iodpropionic acid may be extracted with hot carbon bisulphide or petroleum ether. On distilling off the solvent a discoloured residue remains, from which the acid may be obtained in colourless crystals by recrystallisation from carbon bisulphide.

$$\underset{\text{Glyceric Acid}}{CH_2(OH).CH(OH).COOH} + 3HI = \underset{\beta\text{-Iodpropionic Acid.}}{CH_2I.CH_2.COOH} + 2H_2O + 2I$$

Properties.—Colourless pearly laminae; m.p. 83·5°; slightly soluble in cold, readily in hot water and in alcohol.

PREPARATION LXXVIII.

α-Propenyl Dichlorhydrin, $C_3H_6Cl_2O = CH_2Cl.CH(OH).CH_2Cl$ (*Dichlorhydrin.*)

Literature.—Berthelot (1854) Ann. Ch. Phys. (3) 41, 296; Reboul (1860), Ann. Ch. Phys. (3) 60, 1; Carius (1862), Ann. Ch. Pharm. 122, 73; Claus (1873), Ann Ch. Pharm. 168, 42.

100 grms. anhydrous glycerin.
250 „ chloride of sulphur. (See p. 114.)

Two hundred and fifty grms. chloride of sulphur are slowly added in small quantities from a tap funnel to 100 grms. anhydrous glycerin (dehydrated at 175°) contained in a retort, which is connected with a reflux condenser.* During the process the contents of the retort are well shaken. The reaction is completed on the brine-bath until the evolution of hydrochloric acid has nearly ceased. The condenser is now removed, and the mass again heated until all sulphur dioxide and hydrochloric acid are expelled. The product of the reaction which becomes semi-solid on cooling is extracted with 2–3 times the volume of ether. The ethereal solution is filtered from sulphur and the ether distilled. A liquid remains which may be purified by repeated rectification.

$$\underset{\text{Glycerin.}}{CH_2OH.CH(OH).CH_2(OH)} + 2S_2Cl_2 =$$
$$\underset{\text{α-Dichlorhydrin.}}{CH_2Cl.CH(OH).CH_2Cl} + 2HCl + SO_2 + 3S$$

Properties.—Colourless liquid with an ethereal smell; b. p. 175·8—176·3°; sp. gr. 1·383 at 0°.

PREPARATION LXXIX.

UREA, $CH_4ON_2 = CO<^{NH_2}_{NH_2}$

(*Carbamide.*)

LITERATURE.—Wöhler (1828), Pogg. Ann. 12, 253, Berz. Jahresb. 12, 226; Clemm (1848), Ann. Ch. Pharm. 66, 382.

50 grms. potassium cyanide (pure).[1]
140 „ red oxide of lead.
50 „ ammonium sulphate.

Fifty grms. of pure potassium cyanide are heated in an iron dish or tray over the blow-pipe until it fuses quietly without the application of too strong a heat. To the liquid mass 140 grms. of red oxide of lead are gradually added in small quantities, and the whole again fused for a short time. When the reduced lead has collected at the bottom of the vessel, the liquid mass is poured off on to an iron plate and allowed to cool. It solidifies and is powdered up. It is then dissolved in about 200 c.c. cold water, the aqueous solution of potassium cyanate filtered, and a concentrated solution of 50 grms. neutral

[1] The success of this preparation depends on the purity of the potassium cyanide.

ammonium sulphate added to the filtrate. The liquid is evaporated to dryness on the water-bath, the mass being stirred to prevent the formation of a surface crust. The cooled residue is powdered up and extracted with absolute alcohol, which dissolves out the urea. On distilling off the alcohol, the solid greenish residue is purified by recrystallisation from alcohol with the addition of animal charcoal.

$$\underset{\text{Potassium Cyanide}}{4KCN} + \underset{\text{Lead Oxide}}{Pb_3O_4} = \underset{\text{Potassium Cyanate.}}{4CNOK} + 3Pb$$

$$(NH_4)_2SO_4 + 2KCNO = \underset{\text{Ammonium Cyanate.}}{2CNO.NH_4} + K_2SO_4$$

$$CNO.NH_4 = \underset{\text{Carbamide.}}{CO(NH_2)_2}$$

Properties.—Colourless prisms; m. p. 131°, easily soluble in water, scarcely soluble in ether.

PREPARATION LXXX.

THIOUREA, $CH_4SN_2 = CS{<}^{NH_2}_{NH_2}$

(*Thiocarbamide, Sulphourea.*)

LITERATURE.—Reynolds (1869), Chem. Soc. J. 22, 1; Volhard (1874), Journ. prakt. Ch. (2) 9, 10; Claus (1875), An. Ch. Pharm. 179, 113.

50 grms. ammonium sulphocyanide.

Fifty grms. dry ammonium sulphocyanide are melted (at about 160°) in a round-bottomed flask on the oil-bath, and kept at a temperature at which the mass remains just liquid (140—145°) for 5—6 hours. The cooled melt is powdered and ground with two-thirds its weight of cold water, which dissolves unchanged ammonium sulphocyanide, and but little of the thiourea. By dissolving the residue, which has usually a somewhat reddish tint, in hot water, pure sulphourea is obtained on cooling in colourless crystals.

$$\underset{\substack{\text{Ammonium}\\\text{Sulphocyanide}}}{CNS.NH_4} = \underset{\text{Thiourea}}{CS(NH_2)_2}$$

Properties.—Colourless rhombic prisms (from dilute aqueous solution), long silky needles (from concentrated solutions), m. p. 175°. Very slightly soluble in cold water (one part thiourea dissolves in about eleven parts water at the ordinary temperature).

PREPARATION LXXXI.

ALLOXANTIN, $C_8H_4N_4O_7 + 3H_2O$

LITERATURE.—Liebig, Wöhler (1838), Ann. Ch. Pharm. 26, 262.

10 grms. uric acid.
20 „ hydrochloric acid (sp. gr. 1·19 diluted with an equal quantity of water).
$2\frac{1}{2}$ „ potassium chlorate.

Twenty grms. hydrochloric acid are poured over 10 grms. powdered uric acid, and to the mixture previously heated to 35°, $2\frac{1}{2}$ grms. finely powdered potassium chlorate are slowly added in small quantities at a time with constant stirring. When about four-fifths of the chlorate has been added, the uric acid has nearly dissolved, and the liquor has a faint yellow colour. It is diluted with double the volume of water, allowed to stand for about one hour and filtered. The filtrate is saturated with sulphuretted hydrogen, and yields, after being left for 12 hours, crystalline crusts, often of a reddish tint, of alloxantin mixed with sulphur. It is filtered and washed with cold water, and the alloxantin dissolved in a small quantity of hot water and filtered off from the residue of sulphur. On cooling the filtrate, colourless crystals separate out.

$$\underset{\text{Uric Acid}}{C_5H_4N_4O_3} + O + H_2O = \underset{\text{Alloxan}}{C_4H_2N_2O_4} + \underset{\text{Urea}}{CON_2H_4}$$

$$2C_4H_2N_2O_4 + H_2S = \underset{\text{Alloxantin.}}{C_8H_4N_4O_3} + S + H_2O$$

Properties. — Hard colourless crystals, scarcely soluble in cold, more readily in hot water; gives with baryta water a characteristic violet precipitate.

PREPARATION LXXXII.

ALLOXAN, $C_4H_2N_2O_4 = CO\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\rangle CO$

(*Mesoxalylurea.*)

LITERATURE.—Liebig, Wöhler (1838), Ann. Ch. Pharm. 26, 256; Liebig (1868), Ann. Ch. Pharm. 147, 366; E. Fischer (1882), Ann. Ch. Pharm. 215, 310.

10 grms. alloxantin.
10 ,, conc. nitric acid (sp. gr. 1·42).
20 ,, fuming nitric acid (sp. gr. 1·5).

Ten grms. finely powdered alloxantin are added to a mixture of 20 grms. fuming nitric acid (sp. gr. 1.5), and 10 grms. conc. nitric acid (sp. gr. 1·42), and allowed to stand. Slight evolution of nitrous fumes occurs, and the alloxantin, which at first remains at the bottom of the vessel, slowly changes into the more bulky crystals of alloxan, which gradually fill the liquid. The reaction lasts about two days, and is complete when a sample dissolves readily and completely in cold water. The crystalline mass is spread upon a porous plate, thoroughly dried in the air, and freed from traces of nitric acid by heating in a basin on the water-bath until the smell of the acid disappears. Alloxan may be obtained in large

crystals by dissolving the dry product in the smallest quantity of hot water and allowing the solution to evaporate slowly.

$$\underset{\text{Alloxantin}}{C_8H_4N_4O_7} + O = 2\underset{\text{Alloxan.}}{C_4H_2N_2O_4}$$

Properties.—Colourless brilliant crystals, containing four molecules of water of crystallisation, very soluble in water.

APPENDIX.

APPENDIX.

NOTES ON THE PREPARATIONS.

PART I.

PURIFICATION OF ALCOHOL.

Boiling-point Determination.—A standard thermometer, *i.e.* one that has been calibrated and the 0° and 100° points carefully determined, may be had from a scientific-instrument maker. An ordinary thermometer, corrected by a standard thermometer at Kew, will serve equally well. Where the boiling-points of small quantities of liquid have to be determined small vessels must necessarily be used. Short thermometers are made for such purposes, so that the neck of a small distilling-flask may inclose the thread of mercury. For high boiling liquids similar short thermometers, registering from 100° upwards, are made. The correction for barometric pressure is ·043° for every 1 mm. below 760 (Landolt).

PURIFICATION OF ETHER.

Iodoform Reaction.—On heating iodine in presence of caustic potash and certain organic bodies, a characteristic crystalline

yellow substance, iodoform (CHI_3), is formed. This reaction may be used for ascertaining the presence of small quantities of *ethyl alcohol* (in water orether), *acetone* (in wood-spirit or acetic acid), *aldehyde*, &c. It appears that all bodies containing the group $CH_3.CO.C-$ or $CH_3.CH(OH)C-$, or yielding such groups in presence of iodine and potash, give this reaction (Lieben).

PURIFICATION OF BENZENE.

The treatment with conc. sulphuric acid dissolves out small quantities of thiophen, and dissolves and polymerises the olefines usually present in crude coal-tar benzene. Bromine acts more quickly on the paraffins than on benzene. Rapid decolorisation therefore indicates the presence of the former.

PREPARATION I.

Monobromobenzene.—A general property of organic compounds is that one or more atoms of hydrogen are replaceable by a halogen. When the action of Cl. Br. or I. on a hydrocarbon is one of substitution the hydrogen is eliminated in combination with the halogen as hydracid and the halogen takes its place. The reaction proceeds at the ordinary temperature, more quickly at a high temperature and in direct sun-light In case of the homologues of benzene, *e.g.* toluene, the difference of temperature determines whether the hydrogen is replaced in the benzene nucleus or in the side-chain. At a low temperature or in presence of iodine or other substance which acts as a carrier of Cl, *i.e.* readily takes up Cl and parts with it again ($SbCl_3$, $MoCl_3$), the substitution is in the nucleus; at a high temperature the hydrogen is replaced in the side-chain (Prep. XX.). The halogen substitution products of the aromatic group are much more stable, *i.e.* less readily acted on by reagents than those of the fatty series.

PREPARATION II.

Ethyl Benzene.—"Fittig's reaction," so called from its discoverer, is analogous to the synthetical method employed in the preparation of the fatty hydrocarbons (Wurtz). It is generally applicable, and a long series of homologues of benzene have been prepared in this way.

PREPARATION III.

Nitrobenzene.—The formation of nitro-compounds by the action of strong nitric acid is a distinctive property of aromatic compounds. It appears, indeed, that the smaller the relative proportion of C to H in a compound the more readily does it form nitro-substitution products. The number of hydrogen atoms replaceable by the nitroxyl-group (NO_2) is limited; but also depends on the quantity and dilution of the acid and the temperature of nitration. The oxidising action of the *dilute* acid on the side-chain is exemplified in Prep. XL. This is analogous to the action of nitric acid in the fatty series, where both strong and dilute acid have, as a rule, an oxidising action (Preps. LXVIII. and LXXVI.). Nitro-compounds have often a yellow or red colour, are difficultly or not at all volatile, and possess a much higher boiling-point than the corresponding halogen substitution products.

PREPARATION IV.

Aniline.—Fatty and aromatic nitro-compounds are readily reducible with any of the ordinary reducing agents (ammonium sulphide, iron and acetic or hydrochloric acid, zinc and sulphuric, hydriodic acid, &c.). The oxygen of the nitro-group is replaced by hydrogen, and an amido-compound thereby formed. The latter has basic properties, much less marked, however, than the fatty

amines, which more closely resemble ammonia. Thus aniline hydrochloride has an acid reaction. The action of alkaline reducing agents, such as sodium alcoholate on aromatic nitro-compounds, to form azoxy- and azo-compounds, should be noted. Hofmann's reaction may be expressed equationally as follows :—

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5NC + 3KCl + 3H_2O.$$

PREPARATION V.

Acetanilide.—Amido-compounds are readily acted on by glacial acetic acid or acetic anhydride and form acetyl derivatives or acid-amides (Prep. LVIII.). They are stable bodies, distilling without decomposition. Heated with conc. hydrochloric acid or caustic soda they split up into their components. With chlorine, bromine, nitric acid, &c., substitution products are formed.

PREPARATION VI.

Nitracetanilide.—The aromatic amido-compounds cannot be directly nitrated without undergoing decomposition. With the acetyl derivative or salt of the base, where the amido-group is protected by combination with an acid or acid radical, the operation is readily performed. Observe that the "nitroxyl" takes up by preference the ortho- and para-positions to the "amido" group.

PREPARATION VII.

Dinitrobenzene.—By further nitrating benzene with stronger acid, and at a higher temperature, a second "nitroxyl" is introduced. This latter takes up the meta-position to the first. Note the same relative positions of the nitroxyl groups in picric acid (Prep. XVI.). Whereas a second nitroxyl is readily introduced into the aromatic nucleus, the substitution of a third H atom becomes a matter of greater difficulty.

PREPARATION VIII.

Nitraniline.—Ammonium sulphide is selected here as the reducing agent, on the ground that the action is slow, and may be interrupted after one nitroxyl group has been reduced.

PREPARATION IX.

Diethylaniline.—The tertiary aromatic bases, although analogous in composition to the tertiary amines of the fatty group, have, like the primary bases, less basic properties (Prep. IV.), due probably to the negative character of the radical "phenyl" (Ber. 20, 534). The formation of the "nitrosamine" compound described in the footnote to this preparation is characteristic of all secondary amines or imido-compounds. The "nitrosyl" group (NO) takes the place of the hydrogen atom in the imido-group, = NH, to form nitrosamine, = N.NO.

PREPARATION X.

Nitrosodimethylaniline.—The action of nitrous acid on tertiary amines occurs in the case of aromatic compounds only.

PREPARATION XI.

p-Nitrosophenol.—This compound is also formed by the action of nitrous acid on phenol. Liebermann's reaction is only applicable to aromatic "nitroso" compounds or "nitrosamines" of the fatty series.

PREPARATION XII.

Potassium Benzene Sulphonate.—The action of conc. sulphuric acid on aromatic hydrocarbons is analogous to that of conc. nitric acid. One or more hydrogen atoms of the benzene nucleus are replaceable by the sulphoxyl group (SO_3H) and water is

eliminated. The substitution of a second and third H atom becomes a more difficult operation, and the action is brought about by the use of the fuming acid containing a large percentage of SO_3 or in conjunction with P_2O_5. The free sulphonic acid may be obtained by precipitating the lead salt with H_2S, or the barium salt with sulphuric acid and evaporating the filtrate.

PREPARATION XIII.

Phenol.—The replacement of the sulphoxyl group by hydroxyl by fusion with caustic potash is generally applicable to the preparation of this class of bodies (naphthol from naphthalene sulphonic acid, oxyquinoline from quinoline sulphonic acid, &c.). The action of the two alkalis (NaOH.KOH) is not identical. Whereas with potash molecular change may occur, *i.e.* the hydroxyl does not necessarily take the place of the sulphoxyl group (resorcinol is formed from *o*-benzene disulphonic acid), this is not so often observed with caustic soda. The latter has, however, a greater oxidising action, so that, for example, by fusing resorcinol $C_6H_4(OH)_2$ with caustic soda phloroglucinol $C_6H_3(OH)_3$ is formed (Barth, Schreder). The phenols are also formed from halogen substitution products of benzene by fusion with caustic potash. Compare the latter reaction with that of the fatty compounds.

PREPARATION XIV.

Anisol.—A characteristic property of the hydroxyl group (OH) is that the hydrogen is replaceable by alcohol or acid radicals, forming acid and alcohol ethers. This is true of alcohols (Prep. XLIV.), phenols, and acids (Prep. XLII. and LVII.). The phenol ethers are split up into phenol and chloride or iodide of the alcohol radical by heating with HCl or HI to a high temperature (in sealed tubes), $C_6H_5OCH_3 + HI = CH_3I +$

C_6H_5OH. This reaction has been made the basis of a quantitative method for determining the number of methoxyl-groups ($-OCH_3$) present in a compound.

PREPARATION XV.

O- and *p-Nitrophenol.*—Compare the action of nitric acid on benzene.

PREPARATION XVI.

Picric Acid.—The strongly negative or acid character of the H in the hydroxyl group is due to the presence of the three nitroxyl groups. (Compare the di- and trinitro-derivatives of the paraffins.) Picric acid behaves like an organic acid in decomposing the alkaline carbonates to form salts. In this respect it differs from non-substituted phenols, which combine only with the caustic alkalis.

PREPARATION XVII.

Phenolphthalein.—The action of conc. sulphuric acid is that of a dehydrating agent; that is to say, it withdraws the elements of water from the reacting substances. The reaction, which occurs in this way between organic compounds, resulting in the formation of more complicated bodies, in which the carbon atoms form the connecting link, is termed "condensation." The condensation products produced by similar dehydrating agents ($ZnCl_2$, anhydrous oxalic acid, $SnCl_4$, NaOH, &c.) form a large chapter in organic chemistry.

PREPARATION XX.

Benzyl Chloride.—The chlorination of the toluene is conducted at a high temperature, and takes place therefore in the side chain. By continued action the whole of the three hydrogen

atoms of the methyl group may be replaced by chlorine. At the ordinary temperature, or in presence of a little iodine, the substitution occurs in the benzene nucleus.

PREPARATION XXI.

Benzaldehyde.—In addition to the reactions cited at the end of the preparation, the compounds, which benzaldehyde forms with HCN and hydroxylamine are characteristic alike of all aldehydes and ketones. In the former case compounds of the general formula $R^1C\begin{matrix}OH\\CN\end{matrix}$ are produced, which may be readily converted into an oxy-acid containing a carbon atom more than the original compound (Prep. XXIII.). In the latter reaction the hydroxylamine combines (water being eliminated) to form a compound of the general formula $= C : N.OH$. In the case of aldehyde the compound thus formed has received the name of *aldoxime* (aldehyde-oximido) in that of certain ketones *acetoxime* (acetone-oximido), and similarly *glyoxime* and *quinonoxime* (Prep. XI.). A further property of the "carbonyl" group (CO), common to aldehydes and ketones, is that the oxygen atom by the action of PCl_5 is replaceable by two atoms of chlorine. Benzaldehyde yields benzylene chloride, $C_6H_5CHCl_2$. Aldehydes readily form condensation products (Prep. XXXVI.).

PREPARATION XXII.

Benzyl Alcohol.—The action of caustic potash on aldehydes to form alcohol and acid is not equally applicable to fatty aldehydes. In the latter case, especially with the lower members of the series, resinous products are formed.

PREPARATION XXIII.

α-Toluic Acid.—The property of nitrils to yield an acid with the same number of C atoms, by the action of mineral acids or

alkalis, is common to fatty and aromatic compounds (Preps. XLVIII., LXVI.).

PREPARATION XXIV.

Oxybenzaldehyde.—"Reimer's reaction" for the preparation of oxyaldehydes from phenols is applicable to a very large number of monhydric and polyhydric phenols. The substitution of two H atoms by two aldehyde groups sometimes occurs as in the case of resorcinol. An analogous reaction is that of potash and carbon tetrachloride on phenol with the formation of oxybenzoic acid.

PREPARATION XXV.

Acetophenone.—The production of ketones by the dry distillation of certain organic salts (Ca or Ba salts) occurs also in the case of fatty acids. If a formate be one of the salts employed, an aldehyde is obtained thus: $H.COOM^1 + C_6H_5COOM^1 = C_6H_5COH + M_2{}^1CO_3$.

PREPARATION XXVI.

Benzoin.—This preparation affords an interesting example of molecular change and polymerisation produced by the action of potassium cyanide. Furfurol, $C_4H_3O.COH$, forms, under like conditions, a similar compound (furoin). The reducing action of benzoin on Fehling's solution is shared by aldehydes and hydrazines, and also those bodies (the sugars) which, like benzoin, contain the ketone alcohol group, $CO.CH_2(OH)$.

PREPARATION XXVIII.

Benzoyl Chloride.—The substitution of hydroxyl (OH) by Cl, by the action of PCl_3 or PCl_5, applies to all classes of organic compounds, and the fact is therefore made use of in ascertaining the presence of this group.

PREPARATION XXXI.

Benzonitril.—"Letts' reaction" yields in the case of fatty acids mainly the acid amides. Among the numerous other methods by which the nitrils are formed may be mentioned the action of dehydrating agents (P_2O_5. P_2S_5) on the acid amides. By the action of reducing agents on nitrils (Zn and H_2SO_4 and Na on an alcoholic solution of the nitril) the amines are formed, $C_6H_5CN + H_4 = C_6H_5CH_2NH_2$. Benzonitril yields benzylamine. With hydroxylamine the *amidoximes* are obtained, $C_6H_5CN + NH_3O = C_6H_5(NH_2) : NOH$.

PREPARATION XXXII.

Diazobenzene Nitrate.—This reaction, discovered by Griess, is applicable to all amido-compounds of the aromatic series. By using it as an intermediate step, it is possible to substitute hydrogen, the halogens, hydroxyl, cyanogen, and hydrosulphonyl (SH) for the amido-group. It is not, however, always necessary or advisable to isolate the diazo-compound; but to submit the compound in solution to the further action of reagents. The free base, $C_6H_5N : N.OH$, has not yet been obtained pure. Compare the action of nitrous acid on the primary fatty amines.

PREPARATION XXXIII.

Diazoamidobenzene.—This class of compounds may be regarded as intermediate products in the formation of the azoamido-compounds, and are only formed in the case of primary amines. In other cases (action of diazobenzene on phenols in alkaline solution or tertiary bases in faintly acid solution) the azo-compound is directly produced.

PREPARATION XXXIV.

Amidoazobenzene.—This reaction is an interesting example of molecular change induced by the presence of a small quantity of aniline hydrochloride. It appears, however, that the latter actually takes part in the reaction, replacing the group C_6H_5NH in the diazoamido-compound and regenerating a further quantity of the hydrochloride (Ber. 10, 664 and 1156). It should be noted that the N atom of the diazo-compound replaces by preference the hydrogen of the base which is in the para-position to the amido-group. Amidoazobenzene may be considered as the lowest of the series of that large class of colouring matters known as the azo-colours. They consist essentially of aromatic nuclei double-linked by nitrogen atoms, R – N : N – R and R – N : N – R – N : N – R (tetrazo-compounds). Where the hydrogen atoms of the nuclei (benzene and homologues, naphthalene, &c.) are replaced by the amido-group only, basic colouring matters are formed (aniline yellow, chrysoidine); if by sulphoxyl or hydroxyl in addition or alone (and these form the larger class) acid colouring matters are produced. The colours produced in this way are mainly yellow, red, and intermediate shades. By increasing the size of the molecule (tetrazo-compounds) violet and blue shades have been obtained; but as yet no green colour.

PREPARATION XXXV.

Phenylhydrazine.—The action of reducing agents on diazobenzene was first observed by E. Fischer. In addition to $SnCl_2$ other reducing agents ($NaHSO_3$, zinc dust and acetic acid) may be used. The action of phenlhydrazine on the carbonyl group (CO) yields a compound of the general formula $=C:N.HC_6H_5$.

PREPARATION XXXVI.

Cinnamic Acid.—"Perkin's reaction," so-called from its discoverer, is applicable to substituted aromatic aldehydes, on the one hand, and a large number of fatty acids on the other. According to Fittig the reaction proceeds in the following manner, in which the *aldol* condensation first occurs between the acid and the aldehyde, the acetic anhydride acting as dehydrating agent, $C_6H_5COH + CH_3.CO_2Na = C_6H_5CH(OH).CH_2.CO_2Na = C_6H_5CH:CH.CO_2Na + H_2O$. This reaction furnishes a good illustration of condensation.

PREPARATION XXXVII.

Hydrocinnamic Acid.—Note that the use of sodium amalgam in aqueous or alcoholic solution as a reducing agent is widely applicable.

PREPARATION XXXVIII.

Quinoline.—"Skraup's reaction" may be employed in the case of homologues of aniline, also naphthylamine or anthramine. In this way a large number of quinoline derivatives have been prepared. The first stage of the reaction consists probably in the formation of an aldehyde (acrolein) by the dehydrating action of conc. sulphuric acid on glycerin. The formation of quinaldine (methyl-quinoline) from aldehyde and aniline appears to point to this.

PREPARATION XXXIX.

Mesitylene.—This reaction is an example of *condensation* produced by the action of conc. sulphuric acid, and at the same time of the synthetical formation of an aromatic from a fatty compound. Similar condensations occur in the case of non-saturated hydrocarbons (allylene) and mixed ketones (methylethyl ketone yields triethylbenzene).

PREPARATION XL.

Mesitylenic and Uvitic Acid.—The oxidation of the side-chains in aromatic hydrocarbons is a matter of considerable interest, as illustrating the difference of stability of the side-chain and nucleus, and also of the influence which the relative positions of the side-chains exert in presence of oxidising agents. In the first place it may be mentioned that the aromatic nucleus is acted on by the ordinary oxidising agents only with difficulty. The result is usually complete destruction of the nucleus and the formation of carbonic and oxalic acids. On the other hand, side-chains may be partially or completely oxidised to carboxyl (CO_2H) by choosing suitable oxidising agents. The reagents usually employed are chromic acid or potassium dichromate and sulphuric acid, dilute nitric acid and potassium permanganate in acid or alkaline solution. The action of these on the side-chain, when more than one side-chain is present, depends upon their relative position. Thus, for example, chromic acid or potassium dichromate and sulphuric acid completely destroys the compound when the side-chains occupy the ortho-position (Fittig), whereas the para- and meta-compounds yield the corresponding carboxylic acids. This is true also of substituted hydrocarbons with one side-chain, thus meta- and para-nitrotoluol give meta- and para-nitrobenzoic acid. The ortho-compound with the same oxidising agent is completely oxidised. Dilute nitric acid, or potassium permanganate in alkaline solution, may be used in the oxidation of ortho-side-chains; also, on account of their less energetic action, for partial oxidation where only one side-chain is to be converted into carboxyl.

PREPARATION XLI.

Triphenylmethane.—"Friedel and Craft's reaction," thus named from its discoverers, is very widely applicable, not

only in the preparation of aromatic hydrocarbons ; but also in the formations of ketones, &c., by the action of Al_2Cl_6 on the hydrocarbon in presence of $COCl_2$, thus : $2C_6H_6 + COCl_2 = (C_6H_5)_2CO + 2HCl$.

PREPARATION XLII.

Ethyl Benzoate.—This reaction for the preparation of ethereal salts is generally applicable. The mode in which the reaction proceeds is a disputed point. According to Friedel the acid chloride is first formed and reacts upon the alcohol. According to Henry's views, the reaction takes place in several steps as follows: $R'COOH + C_2H_5OH = R'C(OH)_2OC_2H_5$; $R'C(OH)_2OC_2H_5 + HCl = R'C(OH)ClOC_2H_5 + H_2O$; $R'C(OH)ClOC_2H_5 = R'COOC_2H_5 + HCl$. Another general method for preparing ethereal salts is to act on the dry powdered silver salt of the acid with the alcohol iodide (Wurtz).

PART II.

PREPARATION XLIII.

Ethyl Bromide.—The replacement of the hydrogen by halogen in fatty hydrocarbons occurs under like conditions to those of the aromatic series, *i.e.* by the direct action of the halogen. A simpler method, however, is to replace the alcohol *hydroxyl* by halogen by the action of the hydracid (HCl, HBr, HI) or by

that of the phosphorus compound (PCl_3, PBr_3, P_3). It is not requisite to prepare the latter previous to the operation. As in the preparation of ethyl bromide, the bromide of phosphorus is formed in the presence of alcohol and is at once decomposed. The alcohol may be regenerated from the bromide by heating with water alone or with water and PbO in sealed tubes. With ammonia under similar conditions the fatty amines are produced (Hofmann). With caustic alkalis a hydrocarbon of the series CnH2n is formed.

PREPARATION XLIV.

Ethyl Ether.—This class of bodies are the oxides of the alcohol radicals. They are also formed by the action of sodium alcoholate upon the alcoholic iodides (Williamson). In this way mixed ethers, *i.e.* ethers with dissimilar alcohol radicals, may be readily obtained. The ethers are inert bodies from the fact that the whole of the hydrogen present is united to carbon atoms. Note the action of sodium on alcohol and on ether. The ethers are decomposed with PCl_5 into the haloid ethers of the two alcohol radicals. Hydracids, especially HI, have a similar action. The acid ethers or ethereal salts (German "ester") are much less stable, and are readily hydrolysed, *i.e.* decomposed with caustic alkali into alcohol and acid (Prep. XLII.).

PREPARATION XLVI.

Ethyl Orthoformate.—The formation of this compound is analogous to that of the ethers by Williamson's method, *i.e.* by the action of sodium alcoholate upon the iodide of the alcohol radical thus: $C_2H_5ONa + C_2H_5I = C_2H_5OC_2H_5 + NaI$.

PREPARATION XLVII.

Potassium Ethyl Sulphate.—Compare the action of sulphuric acid on alcohol with that of sulphuric acid on phenol (Prep. XVI.).

PREPARATIONS XLVIII. AND XLIX.

Propionitril.—Read what is written on Prep. XXIII. and XXXI.

PREPARATION L.

Ethylene Bromide.—Hydrocarbon groups with double or treble-linked C atoms, whether occurring free (olefines, acetylenes) or forming part of a compound (Prep. XXXVI.), combine directly with the halogens (most readily with bromine) without evolution of gas, also with the hydracids (to form halogen compounds) nascent hydrogen (to form saturated hydrocarbons) and hypochlorous acid (to form oxyhalogen compounds). Caustic alkalis decompose ethylene bromide, removing first one atom of bromine and one atom of hydrogen from the adjoining carbon atom, and, by prolonged action of the alkali, a second atom of carbon and a second atom of hydrogen and acetylene is formed, $C_2H_4Br_2 + KOH = C_2H_3Br + KBr + H_2O$; $C_2H_3Br + KOH = C_2H_2 + KBr + H_2O$.

PREPARATION LI.

Ethylene Glycol.—The behaviour of dihydric alcohols or glycols towards reagents is similar to that of the monhydric alcohols. It is possible to act upon and modify one or both of the carbinol groups. In the first case a compound would be obtained, which, whilst retaining the character of an alcohol, would

also possess in part the properties of a compound formed by a similar action on a monhydric alcohol. Thus from glycol it is possible to derive glycollic acid, $CH_2(OH).COOH$, a body possessing the properties of both alcohol and acid. It should be remembered that the isomeric glycol with both hydroxyls attached to one carbon atom has not been isolated. Where such a body might be expected to be formed the elements of water are eliminated and aldehyde produced.

PREPARATION LII.

Ethylene Chlorhydrin.— S_2Cl_2 acts on the hydroxyl in a similar manner to, but less energetically than, PCl_5, and at the same time more powerfully than HCl.

PREPARATION LIII.

Succinic Acid.—Read Prep. XXIII.

PREPARATION LIV.

Dibromsuccinic Acid.—Whereas the replacement of hydrogen by chlorine usually occurs under ordinary conditions of temperature, the substitution of bromine (having a less affinity for hydrogen) often requires a high temperature and pressure, and the process is therefore carried out in sealed tubes. The water present, by absorbing some of the hydrobromic acid as it is formed, prevents too great an increase of pressure. The presence of bromine and water together may, under certain circumstances, have an oxidising action. In such cases bromine must be used alone.

PREPARATION LV.

Acetaldehyde.—Read what is written on Prep. XXI. Note also the action of ammonia on benzaldehyde and acetaldehyde.

PREPARATION LVI.

Acetyl Chloride.—Read what is written on Prep. XXVIII. Acetyl chloride determines the presence of the hydroxyl group in alcohols and phenols. By their mutual action hydrochloric acid is evolved and the hydrogen of the hydroxyl replaced by *acetyl*, $C_2H_5OH + C_2H_3OCl = C_2H_5O.C_2H_3O + HCl$.

PREPARATION LVII.

Acetic Anhydride.—This class of compounds may be regarded as oxides of acid radicals, just as ether is the oxide of the alcohol radical. Anhydrides may also be prepared by the action of $POCl_3$ on the potassium salt of the acid in presence of excess of the latter.

PREPARATION LVIII.

Acetamide.—Refer to the preparation of benzamide, Prep. XXVIII.

PREPARATION LIX.

Methylamine Hydrochloride.—This compound belongs to the class of fatty organic bases or amines, *i.e.* bodies having basic properties analogous to ammonia, combining therefore with acids to form salts. By replacing one atom of hydrogen in ammonia by an alcohol radical the primary amines are produced by the replacement, in the same way of two atoms of hydrogen the secondary amines see Prep. XI., of three atoms of hydrogen, the tertiary amines. The latter have the property of combining with alcohol iodide to form substituted ammonium iodides. Trimethylamine, $(CH_3)_3N$, yields tetramethylammonium iodide, $(CH_3)_3N.CH_3I$. The action of nitrous acid differentiates the three classes of amines. In the primary amines the amido-group is replaced by hydroxyl (see Prep. XXXII.).

The secondary group form "nitrosamines" (see Prep. IX.); on the tertiary amines nitrous acid has no action (see Prep. X.). Hofmann's reaction for primary amines is applicable to the fatty compounds (Prep. IV.).

PREPARATION LX.

Ethyl Acetate.—Refer to the preparation of ethyl benzoate (Prep. XLII.).

PREPARATION LXI.

Ethyl Acetoacetate.—A similar reaction occurs also with mixed ethereal salts (Ber. 19, 3225, and 20, 589).

PREPARATION LXIII.

Monochloracetic Acid.—The substitution of hydrogen by chlorine is analogous to that of the hydrocarbons. In the homologous fatty acids, as in the present case, the Cl atom replaces the H atom of the C adjoining the carboxyl group.

PREPARATION LXIV.

Glycocoll.—The amido-acids are neutral bodies; but combine with bases, acids, and salts. Nitrous acid has the same action on the amido-group as on the primary amines, forming oxyacids (Prep. LIX., notes). The hydrochloride of glycocoll ether dissolved in water and treated with $NaNO_2$ yields the diazo-acid ether. This is a general reaction for amido-acids of the fatty series (Ber. 17, 959).

PREPARATION LXVI.

Diethyl Malonate.—Read what is written on Prep. XXIII.

PREPARATION LXVII.

Ethylmalonic Acid.—In those compounds in which the group $CO.CH_2.CO$ occurs (Prep. LXI.), both H atoms are successively replaceable by Na. If ethylmalonic ether were acted on by a second atom of sodium and a second molecule of alcohol iodide both H atoms would be replaced by alcohol radicals. It is possible in this way to build up a series of homologous dibasic acids. Note that dibasic acids with both carboxyl groups attached to the same C atom readily lose CO_2 on heating and form the monobasic acid.

PREPARATION LXX.

Ethyl Diethoxalate.—This reaction of Frankland and Duppa consists, in the first place, in the formation of zinc ethyl (by the action of zinc on ethyl iodide), and this reacting on the acid ether replaces the O atom of the one carbonyl group by two (it can also replace it by one) alcohol radicals. The reaction is applicable to ethers of monobasic acids, but not to the homologues of oxalic ether, $C_nH_{2n-2}O_4$. A similar reaction occurs in the case of aldehydes, ketones, and acid chlorides.

PREPARATIONS LXXI. AND LXXII.

Formic Acid and Allyl Alcohol.—Note the different action of oxalic acid on glycerin at different temperatures. The reducing action of formic acid on mercury and silver salts is due to the aldehyde character of the acid, (OH).COH.

PREPARATION LXXIII.

Allyl Iodide.—This reaction is due to the action of HI, or, what amounts to the same, the combined action of iodine and phosphorus on glycerin. It is probable that propenyl tri-iodide is first formed, $CH_2I.CHI.CH_2I$, which decomposes into

$CH_2 : CH.CH_2I + I_2$. With an excess of HI allyliodide is further transformed into propylene, $CH_2 : CH.CH_2I + HI = CH_2 : CH.CH_2 + I_2$, and isopropyl iodide, $CH_2 : CH.CH_3 + HI = CH_3.CHI.CH_3$.

PREPARATION LXXIV.

Propenyl Tribromide.—The bromine has a two-fold action. It acts in the first place by addition, as in the case of ethylene bromide (Prep. L.), and in the second place by substitution replacing the atom of I.

PREPARATION LXXVI.

Glyceric Acid.—Note the oxidation of the carbinol group $CH_2(OH)$ to carboxyl (CO_2H) characteristic of primary alcohols.

PREPARATION LXXIX.

Urea.—Further properties of urea are as follows : It decomposes above its melting-point into biuret and cyanuric acid. Boiled with alkalis, or heated gently with conc. sulphuric acid, it takes up the elements of water, giving off NH_3 and CO_2. It undergoes similar decomposition in putrefying urine. It combines with acids, bases, and salts to form crystallisable compounds. The nitrate and the compound, obtained by adding a solution of mercuric nitrate to urea, are characteristic.

PREPARATION LXXXII.

Alloxan.—The constitution of alloxan has been determined by the following reactions amongst others. It decomposes with caustic soda or potash into mesoxalic acid and urea. It combines with hydroxylamine to form violuric acid (presence of carbonyl group). On further oxidation with dilute nitric acid it loses CO, and yields parabanic acid (oxalyl urea), the constitution of which has been synthetically determined.

I.—Table of the Atomic Weights of the Elements.

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium	Al.	27·04	Molybdenum	Mo.	95·9
Antimony	Sb.	120·29	Nickel	Ni.	58·6
Arsenic	As.	74·9	Niobium	Nb.	93·7
Barium	Ba.	136·86	Nitrogen	N.	14·01
Beryllium	Be.	9·08	Osmium	Os.	195
Bismuth	Bi.	207 5	Oxygen	O.	15·96
Boron	B.	10·9	Palladium	Pd.	106·2
Bromine	Br.	79·76	Phosphorus	P.	30·96
Cadmium	Cd.	111·7	Platinum	Pt.	194·43
Caesium	Cs.	132·7	Potassium	K.	39·03
Calcium	Ca.	39·91	Rhodium	Rh.	104·1
Carbon	C.	11·97	Rubidium	Rb.	85·2
Cerium	Ce.	141·2	Ruthenium	Ru.	103·5
Chlorine	Cl.	35·37	Scandium	Sc.	44
Chromium	Cr.	52·45	Selenium	Se.	78·87
Cobalt	Co.	58·6	Silicon	Si.	28·33
Copper	Cu.	63·18	Silver	Ag.	107·66
Didymium	Di.	145	Sodium	Na.	22·99
Erbium	E.	166	Strontium	Sr.	87·3
Fluorine	F.	19·06	Sulphur	S.	31·98
Gallium	G.	69·8	Tantalum	Ta.	182
Germanium	Ge.	72·75	Tellurium	Te.	127·7
Gold	Au.	196·85	Terbium	Tb.	148·5
Hydrogen	H	1	Thallium	Tl.	204
Indium	In.	113·4	Thorium	Th.	231·96
Iodine	I.	126 54	Tin	Sn.	117·35
Iridium	Ir.	192·5	Titanium	Ti.	50 25
Iron	Fe.	55·88	Tungsten	W.	183·6
Lanthanum	La.	138·5	Uranium	U.	239·8
Lead	Pb.	206·39	Vanadium	V.	51·1
Lithium	Li.	7·01	Ytterbium	Yb.	173·2
Magnesium	Mg.	23·94	Yttrium	Y.	89·6
Manganese	Mn.	54·8	Zinc	Zn.	64·88
Mercury	Hg.	199·8	Zirconium	Zr.	90·4

II.—Table of Specific Gravity and Percentage of Sulphuric Acid in Aqueous Solution. (Kolb.)

Sp. gr. at 15° compared with water at 0° = 1.

Degrees Beaumé	Sp gr $d = 15/0$.	100 parts by weight contain H_2SO_4.	Degrees Beaumé	Sp. gr. $d = 15/0$.	100 parts by weight contain H_2SO_4.
1	1·007	1·9	34	1·308	40·2
2	1·014	2·8	35	1·320	41·6
3	1·022	3 8	36	1·332	43
4	1·029	4 8	37	1·345	44·4
5	1·037	5 8	38	1·357	45·6
6	1 045	6·8	39	1·370	46·9
7	1·052	7·8	40	1 383	48·3
8	1·060	8·8	41	1·397	49·8
9	1·067	9 8	42	1 410	51·2
10	1·075	10 8	43	1·424	52·6
11	1·083	11·9	44	1 438	54·0
12	1 091	13	45	1·453	55·4
13	1·100	14·1	46	1·468	56·9
14	1·108	15 2	47	1 483	58·3
15	1·116	16·2	48	1·498	59·6
16	1·125	17·3	49	1·514	61
17	1·134	18·5	50	1·530	62·5
18	1·142	19·6	51	1·540	64
19	1·152	20·8	52	1·563	65·5
20	1·162	22·1	53	1·580	67
21	1·171	23 3	54	1·597	68·6
22	1·180	24 5	55	1·615	70
23	1·190	25·8	56	1·634	71·6
24	1·200	27·1	57	1·652	73·2
25	1·210	28·4	58	1·671	74·7
26	1·220	29·6	59	1·691	76·4
27	1·231	30·9	60	1·711	78·1
28	1·241	32·2	61	1·732	79·9
29	1·252	33·4	62	1·753	81·7
30	1·263	34·7	63	1·774	84·1
31	1·274	36	64	1·796	86·5
32	1·285	37·4	65	1 81	89·7
33	1·297	38·8	66	1·842	100

III.—Table of Specific Gravity and Percentage of H_2SO_4 in Concentrated Sulphuric Acid. (Lunge and Naef.)

Sp. gr. at 15° compared with water at 4° = 1.

Percent. H_2SO_4.	Sp. gr. $d = 15/4$.	Percent H_2SO_4.	Sp. gr. $d = 15/4$.
90	1·8185	96	1·8406
91	1·8241	97	1·8410
92	1·8294	98	1·8412
93	1·8339	99	1·8403
94	1·8372	100	1·8384
95	1·8390		

IV.—Table of Specific Gravity and Percentage of Nitric Acid in Aqueous Solution. (Kolbe.)

Sp. gr. at 15° compared with water at 0° = 1.

Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.
1·530	100	1·451	77·6	1·363	58	1·237	37·95
1·529	99·5	1·445	76	1·358	57	1·225	36
1·523	97·9	1·442	75	1·353	56 1	1·218	35
1·516	96	1·438	74	1·346	55	1·211	33 8
1·514	95·2	1·435	73	1·341	54	1·198	32
1·509	94	1 434	72·4	1·339	53·8	1·192	31
1·506	93	1·429	71·2	1·335	53	1·185	30
1·503	92	1·423	69·9	1·331	52 3	1·179	29
1·499	91	1·419	69·2	1·323	51	1·172	28
1·495	90	1·414	68	1·317	49·9	1·166	27
1·494	89·5	1·410	67	1·312	49	1·157	25·7
1·488	88	1·405	66	1·304	48	1·138	23
1·486	87·4	1·400	65	1·298	47·1	1·120	20
1·482	86·1	1·395	64	1·295	46·6	1·105	17·4
1·478	85	1·393	63·6	1 284	45	1·089	15
1·474	84	1·386	62	1·274	43·5	1·077	13
1·470	83	1·381	61·2	1·264	42	1 067	11·4
1·467	82	1·374	60	1·257	41	1·045	7·2
1 463	80·9	1·372	59·6	1·251	40	1·022	4
1·460	80	1·368	58 8	1 244	39	1·010	2
1·456	79						

V.—Table of Specific Gravity and Percentage of Hydrochloric Acid in Aqueous Solution.

Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.
1·007	1·5	1·055	11·0	1·116	23·1	1·175	34·7
1·010	2·2	1·060	12	1·125	24·8	1·180	35·7
1·014	2·9	1·067	13·4	1·134	26·6	1·185	36·8
1·019	3·8	1·075	15	1·143	28·4	1·190	37·9
1·022	4·5	1·083	16·5	1·150	29·7	1·194	38·6
1·029	5·8	1·091	18·1	1·152	30·2	1·199	39·8
1·031	6·2	1·094	18·6	1·159	31·5	1·202	40·5
1·036	7·3	1·100	19·9	1·161	32	1·205	41·2
1·044	8·9	1·105	20·9	1·166	33	1·210	42·4
1·052	10·4	1·108	21·5	1·171	33·9	1·212	43

VI.—Table of Specific Gravity and Percentage of Caustic Potash in Aqueous Solution.

Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.
1·009	1	1·166	19	1·374	37	1·590	54
1·017	2	1·177	20	1·387	38	1·604	55
1·025	3	1·188	21	1·400	39	1·618	56
1·033	4	1·198	22	1·412	40	1·630	57
1·041	5	1·209	23	1·425	41	1·642	58
1·049	6	1·220	24	1·438	42	1·655	59
1·058	7	1·230	25	1·450	43	1·667	60
1·065	8	1·241	26	1·462	44	1·681	61
1·074	9	1·252	27	1·475	45	1·695	62
1·083	10	1·264	28	1·488	46	1·705	63
1·092	11	1·276	29	1·499	47	1·718	64
1·101	12	1·288	30	1·511	48	1·729	65
1·110	13	1·300	31	1·525	49	1·740	66
1·119	14	1·311	32	1·539	50	1·754	67
1·128	15	1·324	33	1·553	51	1·768	68
1·137	16	1·336	34	1·565	52	1·780	69
1·146	17	1·349	35	1·578	53	1·790	70
1·155	18	1·361	36				

VII.—Table of Specific Gravity and Percentage of Caustic Soda in Aqueous Solution.

Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.
1·012	1	1·213	19	1·405	37	1·580	54
1·023	2	1·225	20	1·415	38	1·591	55
1·035	3	1·236	21	1·426	39	1·601	56
1·048	4	1·247	22	1·437	40	1·611	57
1·058	5	1·258	23	1·447	41	1·622	58
1·070	6	1·269	24	1·457	42	1·633	59
1·081	7	1·279	25	1·468	43	1·643	60
1·092	8	1·290	26	1·478	44	1·654	61
1·103	9	1·300	27	1·488	45	1·666	62
1·115	10	1·310	28	1·499	46	1·674	63
1·126	11	1·321	29	1·509	47	1·684	64
1·137	12	1·332	30	1·519	48	1·695	65
1·148	13	1·343	31	1·529	49	1·705	66
1·159	14	1·353	32	1·540	50	1·715	67
1·170	15	1·363	33	1·550	51	1·726	68
1·181	16	1·374	34	1·560	52	1·737	69
1·192	17	1·384	35	1·570	53	1·748	70
1·202	18	1·395	36				

VIII.—Table of Specific Gravity and Percentage of Ammonia in Aqueous Solution.

Sp. gr. at 14° compared with water at 14° = 1.

Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.	Sp. gr.	Percentage of NH_3.
·884	36	·905	27	·931	18	·963	9
·886	35	·907	26	·934	17	·967	8
·888	34	·910	25	·938	16	·970	7
·890	33	·913	24	·941	15	·974	6
·892	32	·916	23	·944	14	·979	5
·895	31	·919	22	·948	13	·983	4
·897	30	·922	21	·952	12	·987	3
·900	29	·925	20	·955	11	·991	2
·902	28	·928	19	959	10	·995	1

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